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Fibre Labelling
Polypropylene/polyamide bicomponent - Aquafil

FINAL REPORT
Administrative Arrangement N. 2007-30291
Analysis conducted on behalf of DG ENTERPRISE

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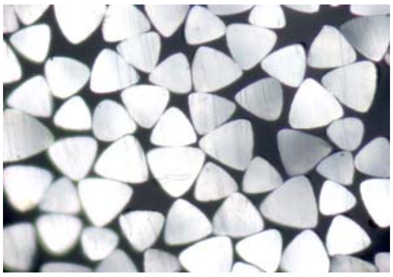


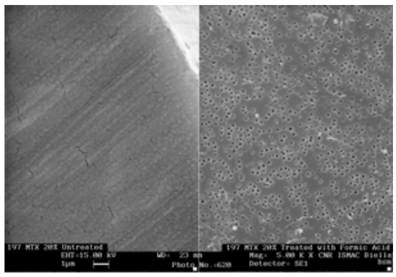

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1. Executive Summary

In November 2005, the European Commission received a petition, presented by Aquafil S.p.A, for the establishment of a new generic fibre name, in accordance with Directive 96/74/EC (currently substituted by Directive 2008/121/EC). The proposed name was propylamidecomposite (PAC) and the suggested definition was the following: "a composite fibre composed of between 10 % and 45 % by mass of polyamide fibrils embedded in polypropylene matrix". On 6th February 2006, the European Commission convened a meeting of the technical expert working group on Textile Labelling, comprised of governmental experts representing each member state. The application was considered justified and therefore, an amendment to the European legislation on textile names (Directive 2008/121/EC) and quantification of binary textile fibre mixtures (Directive 96/73/EC) would subsequently be prepared.

In August 2007, the European Commission's Joint Research Centre (JRC) was entrusted by DG Enterprise (DG ENTR) to conduct experimental work regarding the validity and applicability of the testing methods proposed by the petitioner for the identification and quantification of the new fibre. Results of this study were presented and discussed during the 9th, 10th and 11th technical meetings of the European network of national experts on Textile Labelling (ENNETL), held in Ispra on 20th October 2008, 10th December 2009 and 15th July 2010.

Name and definition

Based on discussions held during the 11th ENNETL meeting and on written consultation with national experts, the name "*polypropylene/polyamide bicomponent*" was chosen for the new fibre, as it fulfils the criteria set up in 2002 by the Commission and the technical experts working group on Textile Labelling. According to these criteria, a generic name should not link the fibre to a specific manufacturer, it should be free of rights and it should inform consumers about the characteristics of the fibre. On the basis of the experimental results and the written opinion of experts, the definition agreed and proposed for the new fibre was: "*a bicomponent fibre composed of between 10 % and 25 % by mass of polyamide fibrils embedded in polypropylene matrix*".

Identification methods

The experiments performed by the JRC and described in this report confirmed that test methods are available for the identification of the new fibre. Identification of PAC can be achieved using Scanning Electronic Microscope (SEM) analysis, after dissolving the polyamide fibrils with formic acid. In order to be able to distinguish PAC from binary mixtures polypropylene (PP) – polyamide (PA), Fourier Transform Infrared Spectroscopy (FT-IR) and Differential Scanning Calorimetry (DSC) can be used.

Parameters for quantification

For quantification purposes, ventilated oven can be used, instead of the vacuum one proposed by the applicant, as statistical evaluation showed that results could be considered equivalent in the two cases. The pre-treatment described in Directive 96/73/EC was proved to be applicable to the new fibre and its established mass loss due to pre-treatment (*b* correction factor) was 0 %. Experts decided to establish the value of 1.00 % for the *agreed allowance* of the new fibre, based on the experimental average value of 0.40 %. PAC was found to be insoluble in methods 1, 2, 5-11 and 14 and the following *d* correction factors were established: 1.00 for methods 1, 2, 5, 6, 8-10, 1.005 for method 11 and 1.01 for methods 7 and 14. Three of these correction factors (for methods 2, 8 and 11) were validated through a collaborative trial at European level on PAC 20 %. PP was proved to be insoluble in methods 1, 3, 5-11, 14 and 16 (*d* factor values 1.00 in all cases) and soluble in method 15. Polyamide 6 (PA6) was shown to be insoluble in methods 5 and 10 (*d* factor values 1.00 and 1.01, respectively) and soluble in methods 3, 7, 11 and 16. Experts agreed that all these parameters shall be inserted in Directive 96/73/EC, apart from the *d* correction factors for PA which were measured just on PA6.

Quantification methods (PA in PAC)

For the quantification of PA in PAC, three methods were proposed by the applicant: the first one was based on hydrolysis of the sample with hydrochloric acid solution, the second one on DSC analysis and the third one on FT-IR analysis. In addition, a series of chemical dissolution methods were tested. The PA content of PAC samples was determined *via* elemental analysis and these results were used as reference values to judge the accuracy of all the other methods.

The hydrolysis method was considered not accurate and very time-consuming. The DSC and FT-IR methods gave results in good agreement with the reference values, but showed the disadvantage of requiring the availability of standards of PAC of various PA contents. For these reasons, none of the aforementioned methods was considered by the JRC and the network of national experts suitable to quantify PA in PAC. Among the tested chemical methods, method 16 of Directive 96/73/EC was proved to be the most accurate and non time-consuming. It was, therefore, proposed by the JRC and agreed by experts as the suitable method to quantify PA in PAC.

Quantification methods (binary mixtures)

For the quantification of PAC in binary mixtures, manual separation is an adequate technique, whenever applicable. In the case of binary mixtures of PAC with PA or PP, several alternative methods were studied. In order to judge their accuracy, results were compared to the ones obtained *via* manual separation. The DSC method did not provide accurate quantification of these binary mixtures.

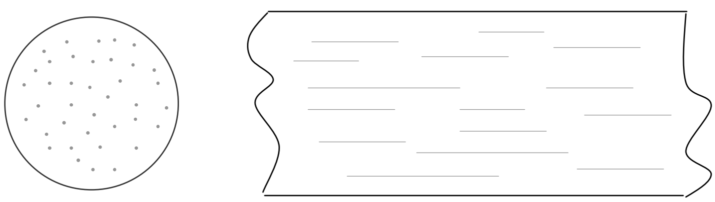
In the case of binary mixtures PP/PAC, method 16 of Directive 96/73/EC was proved to be accurate. PA inside PAC could be solubilised by 90 % formic acid solution under the conditions of this method. However, the quantification of binary mixtures can be achieved only if the PA content of PAC is known. In an attempt to try to overcome this problem, a densitometric approach was used to separate PAC from PP/PAC binary mixtures, to allow the quantification of PA content in it; however, several problems were experienced leading to lack of repeatability.

Concerning binary mixtures PA/PAC, method 11 of Directive 96/73/EC was considered very accurate and was proposed by the JRC for quantification purposes. Under the conditions of this method, only the PA fibres in the binary mixture were solubilised by 75 % sulphuric acid and not the PA fibrils inside PAC. As agreed during the 10^{th} ENNETL meeting, the JRC organised a collaborative trial to validate method 11, in accordance with the rules laid down in ISO 5725 (1994). Loop twisted carpet samples of three levels of concentration were used and 17 European laboratories took part in the exercise. On the basis of successful results, experts agreed that the field of application of method 11 in Directive 96/73/EC shall be extended to the quantification of the binary mixtures PA/PAC, with the addition of PAC as an insoluble fibre. Moreover, the modified washing procedure, needed to achieve a correct quantification of binary mixtures with high percentages of PA fibres, shall be added in the method's description together with the established precision of the analytical method, expressed as reproducibility limit (2 %).

2. Introduction

In November 2005, the company Aquafil S.p.A requested to the European Commission the establishment of a new generic fibre name under Directive 96/74/EC on textile names [1], now substituted by Directive 2008/121/EC [2], as they claimed the novelty of their new fibre. The new fibre was specifically designed for carpet applications, for which durability and high appearance retention is needed. The request was submitted on the basis of several aspects suggested by the petitioner, such as the fact that the new fibre presents high permanent stain resistance; the use of polluting solvents and staining resistance products could, therefore, be avoided. Moreover, dyeability, intrinsic bleach resistance and good mechanical performances are considered to be advantages of the new fibre. The applicant considered that no existing fibre definitions could be used due to the new chemical composition of the fibre; therefore, requested a new name with the following definition: "a composite fibre composed of between 10 % and 45 % by mass of polyamide fibrils embedded in polypropylene matrix". The proposed name was propylamidecomposite (PAC).

PAC is made by a combination of two different incompatible polymers, polypropylene (hydrophobic properties) and polyamide (hydrophilic properties). It is produced *via* a blend reactive spinning process, which gives a characteristic microstructure of "islands-in-the-sea" type. The fibre is composed of short fibrils of polyamide (PA), embedded inside a polypropylene (PP) matrix. The fibrils have a length of up to 1 mm and a diameter of up to 0.5 μm. Each filament contains millions of reinforcing fibrils. During the reactive spinning process, by means of special additives (compatibiliser) and of specific temperatures in the melting zones, copolymers are produced at the boundaries, so that the strong chemical links avoid fibrillation of the two incompatible materials. PAC currently in production contains around 20 % of polyamide 6 (PA6).



"Islands-in-the-sea" structure (cross-section and longitudinal view).

According to the producer, the physical and chemical interaction of the components leads to the creation of a mix of properties that is not possible to achieve by using physical mixtures of the components. In fact, on the one hand, polypropylene fibres are characterised by high chemical inertia and very low moisture absorption, presenting, however, poor mechanical properties. On the other hand, polyamide fibres provide excellent mechanical properties and very good viscoelastic properties; however, their yarns are easily stained. The petitioner suggested that the uniqueness of the new fibre is that it combines the best properties of each polymer (very high stain resistance together with good mechanical performances), making it different from the existing fibres and interesting for the end-consumer. In addition, tests carried out at the ITCF Institute of Denkendorf (D) demonstrated that the fibre is characterised by good dyeability properties. It can be dyed using commercially available dyestuffs, with the resulting colour presenting good light and water fastness. Although the fibre is dyeable, at the same time it is claimed to be intrinsically inert against all common staining products. Its stain resistance remains even after washing, cleaning, abrasion or heating. It is, therefore, considered suitable to solve the major problem currently affecting the textile floor-covering market, i.e. hygiene and easy maintenance. Moreover, the inert polyolefin shield protects polyamide fibrils from chemical attack, such as bleach containing solutions.

The application was discussed for the first time on 6th February 2006 during a meeting of the technical expert working group on Textile Labelling, composed of member states' governmental experts associated with the Committee for Directives relating to Textile Names and Labelling. Based on the following agreed set of criteria, the group of experts considered that the petition was justified:

1. the new fibre should be radically different from other fibres by chemical composition and/or by manufacturing route and production process;
2. fibre characteristics can be taken into account, but need to be examined on a case by case basis;
3. the new fibre should be detectable and distinguishable from other fibres by standardised test methods;
4. consumer relevance should be shown by active commercial use of the fibre;
5. a new name is justified only if the fibre cannot be classified into existing groups.

The group judged that experimental work was needed to verify the applicability of the proposed analytical methods for identifying and quantifying PAC in blends. In fact, validated test methods, enabling market surveillance authorities in member states to determine the composition of textile products containing the new fibre, should be established at European level. An amendment to the European legislation on textile names (Directive 2008/121/EC) and quantification of binary textile fibre mixtures (Directive 96/73/EC [3]) would subsequently be prepared.

In August 2007, the European Commission's Joint Research Centre (JRC) was entrusted by DG Enterprise (DG ENTR) to conduct experimental work to verify the validity and applicability of the testing methods proposed by the applicant for the identification and quantification of the new fibre (Administrative Arrangement between JRC and DG ENTR, JRC Ref. Contract n. 30291).

3. Background information

The work plan included the verification of the applicability of the pre-treatment described in Directive 96/73/EC to the new fibre, the determination of the percentage mass loss due to pre-treatment (*b*), the *agreed allowance* and the solubility properties of PAC with the determination of its correction factors *d*. The most important issue concerned the verification of identification and quantification methods proposed by Aquafil (based on microscopic and FT-IR analysis, chemical dissolution methods and Differential Scanning Calorimetry).

The JRC collaborated with Aquafil to identify relevant samples for the experimental phase, taking into consideration possible range of compositions in blends. In view of the foreseen use of PAC in carpet applications, binary and ternary mixtures with PA and PP were judged as the most interesting ones. Aquafil was asked to provide various samples of pure PAC with different PA6 content, together with binary and ternary mixtures with PA6 and PP. Table 1 lists all samples received from Aquafil, while Table 2 shows the samples' composition according to the petitioner, based on linear density measurements (dtex[1]). The samples used in this project were both yarns and carpets, received by the JRC from February 2007 until March 2010. Samples **160, 162** – **167** were used only for preliminary testing. Sample **160** was not included in the final experimental study, as it was proved to be non-resistant to the experimental conditions. Samples **234** – **257** were carpets prepared by Aquafil for testing purposes in a small pilot plant, using both the loop and cut structure. Apart from samples listed in Table 1, sample **113** was also used in this project; it is composed of 100 % PP (yarn from bobbin), has a linear density of 121 dtex and was received by the JRC in the frame of a previous project. Samples **280**, **282** – **284** were used for the collaborative trial organised by the JRC at European level for the validation of the method to quantify binary mixtures PA/PAC and of three correction factors *d* for PAC.

[1] **dtex** is a unit to express linear density, numerically equal to the weight in grams of 10 000 meters of yarn, fibre or other textile strand.

Table 1: Samples received from Aquafil.

JRC code	composition	nominal PA6 %	sample type	manufacturing type	colour	arrival date	TiO_2
160	100 % PAC	20 %	bobbin	interlaced	white	5/2/07	Yes
162	100 % PAC	7 % DU*	carpet - cut	twisted	grey	5/2/07	Yes
163	100 % PAC	15 % DU	carpet - cut	twisted	light green	5/2/07	Yes
164	100 % PAC	20 % BT**	carpet - cut	twisted	green	5/2/07	No
165	100 % PAC	20 % DU	carpet - cut	twisted	light green	5/2/07	Yes
166	100 % PAC	20 % 2-DU	carpet - cut	twisted	grey	5/2/07	Yes
167	100 % PAC	30 % DU	carpet - cut	twisted	green	5/2/07	Yes
184	100 % PA6	-	granules	-	white	12/6/07	No
185	100 % PP	-	granules	-	white	12/6/07	No
186	100 % PP	-	bobbin	interlaced	white	27/7/07	No
187	100 % PP	-	bobbin	interlaced	dark yellow	27/7/07	No
188	100 % PA6	-	bobbin	interlaced	grey	27/7/07	Yes
189	100 % PA6	-	bobbin	interlaced	white	27/7/07	Yes
192	100 % PP	-	bobbin	interlaced	white	28/11/07	No
193	100 % PA6	-	bobbin	interlaced	white	28/11/07	Yes
194	100 % PA66	-	bobbin	interlaced	white	28/11/07	Yes
195	100 % PAC	5 %	bobbin	interlaced	white	28/11/07	No
196	100 % PAC	10 %	bobbin	interlaced	white	28/11/07	No
197	100 % PAC	20 %	bobbin	interlaced	white	28/11/07	No
198	100 % PAC	30 %	bobbin	interlaced	white	28/11/07	No
199	100 % PAC	40 %	bobbin	interlaced	white	28/11/07	No
200	PA6/PAC	10 %	bobbin	interlaced	white	28/11/07	Yes / No
201	PA6/PAC	10 %	bobbin	twisted	white	28/11/07	Yes / No
202	PA6/PAC	20 %	bobbin	interlaced	white	28/11/07	Yes / No
203	PA6/PAC	20 %	bobbin	twisted	white	28/11/07	Yes / No
204	PA6/PAC	30 %	bobbin	interlaced	white	28/11/07	Yes / No
205	PA6/PAC	30 %	bobbin	twisted	white	28/11/07	Yes / No
206	PA6/PAC	40 %	bobbin	twisted	white	28/11/07	Yes / No
207	PP/PAC	10 %	bobbin	interlaced	white	28/11/07	No / No
208	PP/PAC	10 %	bobbin	twisted	white	28/11/07	No / No
209	PP/PAC	20 %	bobbin	interlaced	white	28/11/07	No / No
210	PP/PAC	20 %	bobbin	twisted	white	28/11/07	No / No
211	PP/PAC	30 %	bobbin	interlaced	white	28/11/07	No / No
212	PP/PAC	30 %	bobbin	twisted	white	28/11/07	No / No
213	PP/PAC	40 %	bobbin	twisted	white	28/11/07	No / No
214	PA6/PAC/PP	10 %	bobbin	interlaced	white	28/11/07	Yes / No / No
215	PA6/PAC/PP	10 %	bobbin	twisted	white	28/11/07	Yes / No / No
216	PA6/PAC/PP	20 %	bobbin	interlaced	white	28/11/07	Yes / No / No
217	PA6/PAC/PP	20 %	bobbin	twisted	white	28/11/07	Yes / No / No
218	PA6/PAC/PP	30 %	bobbin	interlaced	white	28/11/07	Yes / No / No
219	PA6/PAC/PP	30 %	bobbin	twisted	white	28/11/07	Yes / No / No
220	PA6/PAC/PP	40 %	bobbin	twisted	white	28/11/07	Yes / No / No
233	100% PAC	20 %	bobbin	interlaced	white	25/11/08	Yes

* DU dull (with TiO_2)

** BT bright (without TiO_2)

JRC code	composition	nominal PA6 %	sample type	manufacturing type	colour	arrival date	TiO_2
234	PA6/PAC	30 %	carpet - 1/10 loop	twisted	beige + white	24/2/09	Yes / No
235	PA6/PAC	20 %	carpet - 1/10 loop	twisted	beige + white	24/2/09	Yes / No
236	PA6/PAC	10 %	carpet - 1/10 loop	twisted	beige + white	24/2/09	Yes / No
237	PA6/PAC	30 %	carpet - 1/10 loop	interlaced	beige + white	24/2/09	Yes / No
238	PA6/PAC	20 %	carpet - 1/10 loop	interlaced	beige + white	24/2/09	Yes / No
239	PA6/PAC	10 %	carpet - 1/10 loop	interlaced	beige + white	24/2/09	Yes / No
240	PA6/PAC	30 %	carpet - 1/10 cut	twisted	beige + white	24/2/09	Yes / No
241	PA6/PAC	20 %	carpet - 1/10 cut	twisted	beige + white	24/2/09	Yes / No
242	PA6/PAC	10 %	carpet - 1/10 cut	twisted	beige + white	24/2/09	Yes / No
243	PA6/PAC	30 %	carpet - 1/10 cut	interlaced	beige + white	24/2/09	Yes / No
244	PA6/PAC	20 %	carpet - 1/10 cut	interlaced	beige + white	24/2/09	Yes / No
245	PA6/PAC	10 %	carpet - 1/10 cut	interlaced	beige + white	24/2/09	Yes / No
246	PP/PAC	30 %	carpet - 1/10 loop	twisted	black + white	24/2/09	Yes / No
247	PP/PAC	20 %	carpet - 1/10 loop	twisted	black + white	24/2/09	Yes / No
248	PP/PAC	10 %	carpet - 1/10 loop	twisted	black + white	24/2/09	Yes / No
249	PP/PAC	30 %	carpet - 1/10 loop	interlaced	black + white	24/2/09	Yes / No
250	PP/PAC	20 %	carpet - 1/10 loop	interlaced	black + white	24/2/09	Yes / No
251	PP/PAC	10 %	carpet - 1/10 loop	interlaced	black + white	24/2/09	Yes / No
252	PP/PAC	30 %	carpet - 1/10 cut	twisted	black + white	24/2/09	Yes / No
253	PP/PAC	20 %	carpet - 1/10 cut	twisted	black + white	24/2/09	Yes / No
254	PP/PAC	10 %	carpet - 1/10 cut	twisted	black + white	24/2/09	Yes / No
255	PP/PAC	30 %	carpet - 1/10 cut	interlaced	black + white	24/2/09	Yes / No
256	PP/PAC	20 %	carpet - 1/10 cut	interlaced	black + white	24/2/09	Yes / No
257	PP/PAC	10 %	carpet - 1/10 cut	interlaced	black + white	24/2/09	Yes / No
258	100 % PA6	-	bobbin	interlaced	white	16/3/09	Yes
259	100 % PP	-	bobbin	interlaced	black	16/3/09	Yes
260	100 % PP	-	bobbin	interlaced	white	19/11/09	Yes
261	100 % PP	-	bobbin	interlaced	white	19/11/09	Yes
262	100 % PA6	-	bobbin	interlaced	white	19/11/09	Yes
263	100 % PA6	-	bobbin	interlaced	white	19/11/09	Yes
264	100 % PA6	-	bobbin	interlaced	white	19/11/09	Yes
265	PAC	20 %	bobbin	interlaced	white	19/11/09	Yes
266	PAC	40 %	bobbin	interlaced	white	19/11/09	Yes
267	PA6/PAC	20 %	carpet - loop	twisted	white	19/11/09	Yes / Yes
268	PA6/PAC	20 %	carpet - loop	twisted	white	19/11/09	Yes / Yes
269	PA6/PAC	20 %	carpet - loop	twisted	white	19/11/09	Yes / Yes
270	PA6/PAC	40 %	carpet - loop	twisted	white	19/11/09	Yes / Yes
271	PP/PAC	20 %	carpet - loop	twisted	white	19/11/09	Yes / Yes
272	PP/PAC	20 %	carpet - loop	twisted	white	19/11/09	Yes / Yes
273	PP/PAC	20 %	carpet - loop	twisted	white	19/11/09	Yes / Yes
274	PP/PAC	40 %	carpet - loop	twisted	white	19/11/09	Yes / Yes
275	100 % PP	-	bobbin	interlaced	white	19/03/10	No
276	100 % PP	-	bobbin	interlaced	white	19/03/10	No
277	100 % PA6	-	bobbin	interlaced	white	19/03/10	Yes
278	100 % PA6	-	bobbin	interlaced	white	19/03/10	Yes
279	100 % PA6	-	bobbin	interlaced	white	19/03/10	Yes
280	PAC	20 %	bobbin	interlaced	white	19/03/10	Yes
281	PAC	40 %	bobbin	interlaced	white	19/03/10	Yes
282	PA6/PAC	20 %	carpet - loop	twisted	white	19/03/10	Yes / Yes
283	PA6/PAC	20 %	carpet - loop	twisted	white	19/03/10	Yes / Yes

JRC code	composition	nominal PA6 %	sample type	manufacturing type	colour	arrival date	TiO_2
284	PA6/PAC	20%	carpet - loop	twisted	white	19/03/10	Yes / Yes
285	PA6/PAC	40%	carpet - loop	twisted	white	19/03/10	Yes / Yes
286	PP/PAC	20%	carpet - loop	twisted	white	19/03/10	No / Yes
287	PP/PAC	20%	carpet - loop	twisted	white	19/03/10	No / Yes
288	PP/PAC	20%	carpet - loop	twisted	white	19/03/10	No / Yes
289	PP/PAC	40%	carpet - loop	twisted	white	19/03/10	No / Yes

Table 2: Samples' composition based on linear density measured by Aquafil.

JRC code	composition	nominal PA6 %	filament number	linear density (dtex)	PA6/PP/PAC % *	linear density (dtex)	PA6/PP/PAC % **
				theoretical values		experimental values	
160	100 % PAC	20 %	60	1150	-	-	-
186	100 % PP	-	42	900	-	-	-
187	100 % PP	-	42	650	-	-	-
188	100 % PA6	-	42	700	-	-	-
189	100 % PA6	-	42	700	-	-	-
192	100 % PP	-	60	1178	-	1183.9	-
193	100 % PA6	-	64	1331	-	1335.5	-
195	100 % PAC	5 %	60	1187	-	1150	-
196	100 % PAC	10 %	60	1168	-	1186.9	-
197	100 % PAC	20 %	60	1178	-	1201.1	-
198	100 % PAC	30 %	60	1203	-	1218.7	-
199	100 % PAC	40 %	60	1206	-	1220.3	-
200	PA6/PAC	10 %	-	2545	50.2 / 49.8	2553.3	52.9 / 47.1
201	PA6/PAC	10 %	-	2590	53.3 / 46.7	2586.6	52.9 / 47.1
202	PA6/PAC	20 %	-	2598	50.0 / 50 0	2588.1	52.6 / 47.4
203	PA6/PAC	20 %	-	2653	52.9 / 47.1	2595.4	52.6 / 47.4
204	PA6/PAC	30 %	-	2605	49.5 / 50.5	2578.4	52.3 / 47.7
205	PA6/PAC	30 %	-	2655	51.9 / 48.1	2627.5	52.3 / 47.7
206	PA6/PAC	40 %	-	2659	51.7 / 48.3	2534.3	52.3 / 47.7
207	PP/PAC	10 %	-	2400	50.2 / 49.8	2348.7	49.9 / 50.1
208	PP/PAC	10 %	-	2412	50.2 / 49.8	2432.1	49.9 / 50.1
209	PP/PAC	20 %	-	2427	50.0 / 50 0	2379.9	49.6 / 50.4
210	PP/PAC	20 %	-	2461	50.0 / 50 0	2403.3	49.6 / 50.4
211	PP/PAC	30 %	-	2482	49.5 / 50.5	2431.5	49.3 / 50.7
212	PP/PAC	30 %	-	2466	49.5 / 50.5	2497.0	49.3 / 50.7
213	PP/PAC	40 %	-	2508	49.4 / 50.6	2394.6	49.2 / 50.8
214	PA6/PAC/PP	10 %	-	3768	36.2 / 31.8 / 32.0	3752.9	36.0 / 31.9 / 32.0
215	PA6/PAC/PP	10 %	-	3912	36.2 / 31.8 / 32.0	3821.1	36.0 / 31.9 / 32.0
216	PA6/PAC/PP	20 %	-	3773	36.1 / 32.0 / 32.0	3734.6	35.9 / 31.8 / 32.3
217	PA6/PAC/PP	20 %	-	3807	36.1 / 32.0 / 32.0	3818.1	35.9 / 31.8 / 32.3
218	PA6/PAC/PP	30 %	-	3767	35.9 / 32.4 / 31.7	3799.9	35.7 / 31.7 / 32.6
219	PA6/PAC/PP	30 %	-	3895	35.9 / 32.4 / 31.7	3904.5	35.7 / 31.7 / 32.6
220	PA6/PAC/PP	40 %	-	3756	35.8 / 32.5 / 31.7	3778.4	35.7 / 31.7 / 32.6

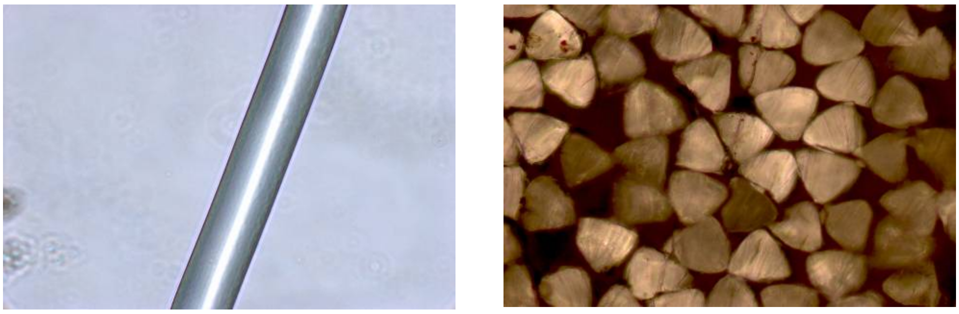
* Percentages calculated on the basis of theoretical values of linear density of pure PA6, PP and PAC used to prepare the mixtures
** Percentages calculated on the basis of experimental values of linear density of pure PA6, PP and PAC used to prepare the mixtures

4. Test methods for identification of the new fibre

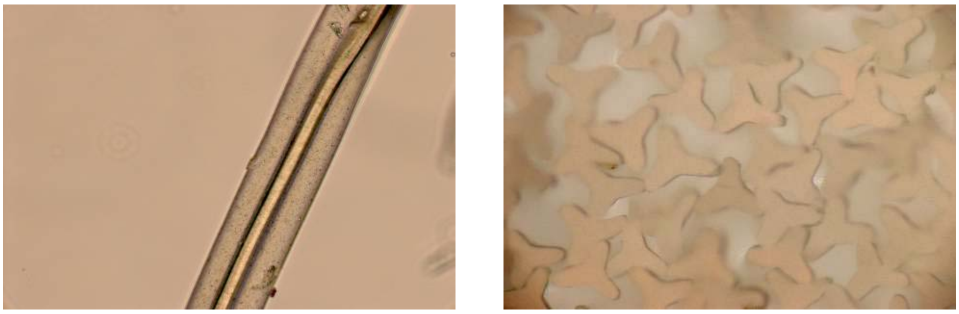
The methods proposed by the applicant for identifying PAC were based on Scanning Electronic Microscope (SEM) analysis, Fourier Transform Infrared Spectroscopy (FT-IR) and Differential Scanning Calorimetry (DSC) (see Annex I). In this section results obtained with these techniques, plus optical microscopic analysis, are reported. Complete results are shown in Annexes II, III and IV. It has to be highlighted that, due to its composition, the new fibre has to be distinguishable not only from all the other fibres, but also from binary mixtures PP - PA. In the following, these mixtures will be referred to as "physical mixtures" PP - PA to stress the difference with the new fibre, which contains polyamide fibrils in polypropylene matrix with "islands-in-the-sea" structure.

4.1 Microscopy

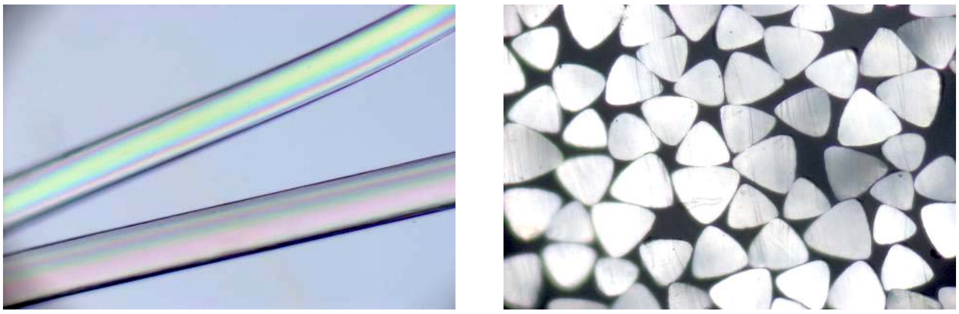
The optical microscopic analysis of pure PP, PA6 and PAC 20 % are shown in Fig. 1. A Zeiss microscope model Axioskop 2 Mat was used and analyses were performed using transmitted light. Glyceryl triacetate (refractive index: 1.158) was used as mounting medium. Photos of samples received from Aquafil, analysed by microscopy for a preliminary characterisation, are reported in Annex II.



Polypropylene



Polyamide 6

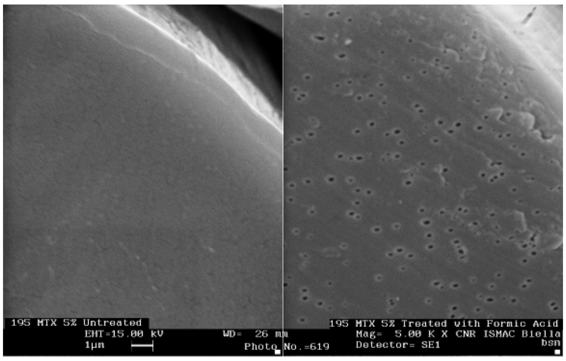


PAC 20 %

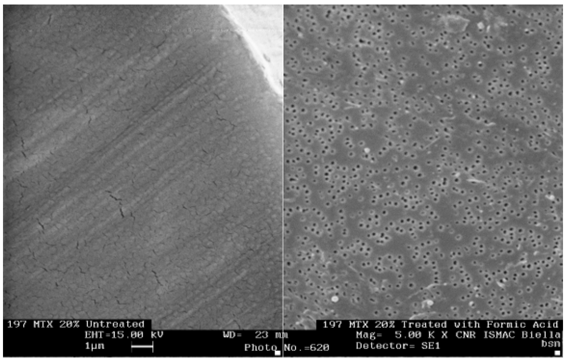
Fig. 1: Longitudinal and cross section analysis of PP, PA6 and PAC (20x).

As evident from the photos reported as an example in Fig. 1, it can be concluded that PAC cannot be identified by optical microscopy since it has the same appearance as polypropylene fibres.

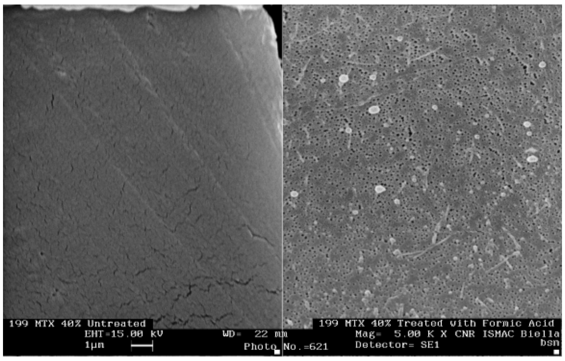
The bicomponent nature of the new fibre and its microstructure of “islands-in-the-sea” type can be identified by Scanning Electron Microscope (SEM) analysis. In fact, after dissolving PA6 inside the new fibre with 98-100 % formic acid at room temperature for 15 minutes, the cross-section analysis showed several holes where fibrils of PA6 were present (Fig. 2).



(a)



(b)



(c)

Fig. 2: SEM cross-section of PAC containing:
a) 5 % PA6 (sample **195**); b) 20 % PA6 (sample **197**); c) 40 % PA6 (sample **199**).

It can be clearly observed that the number of holes increased with the increasing content of PA6 inside PAC. SEM analyses were performed by the Italian National Research Council (Consiglio Nazionale delle Ricerche, CNR), Biella, Italy.

4.2 Fourier transform infrared spectroscopy

The nature of the new fibre can be proved by means of Fourier transform infrared spectroscopy (FT-IR). All spectra were acquired using Attenuated Total Reflectance (ATR) mode with a Perkin Elmer instrument (FT-IR spectrometer spectrum 2000). Spectra were acquired in the scan range 4000.00 - 650.00 cm^{-1}, with a resolution of 4.00 cm^{-1} and a total of 4 scans. The FT-IR spectra of pure PA6, PP and PAC 20 % are shown below (Figs. 3-5). Samples were analysed without any preparation. FT-IR spectra of Aquafil samples are reported in Annex III.

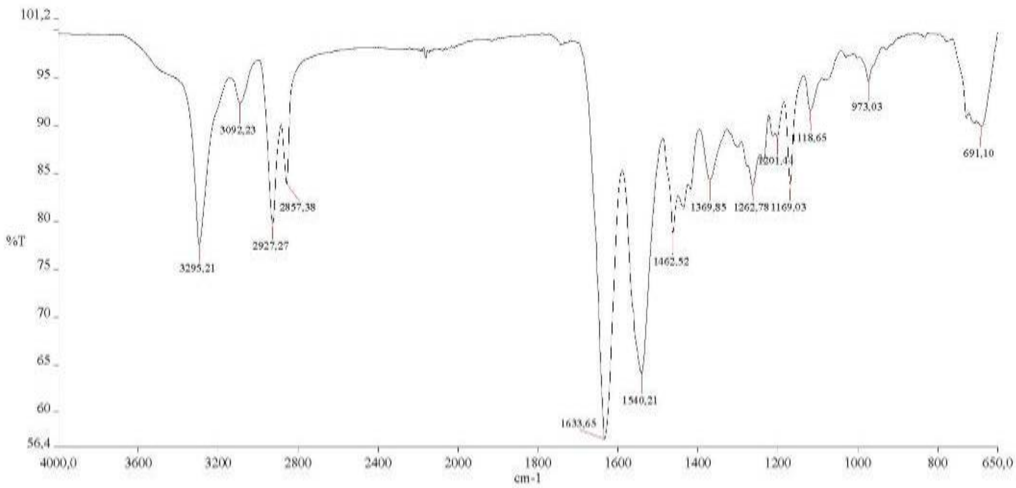


Fig. 3: FT-IR spectrum of PA6 (sample **193**).

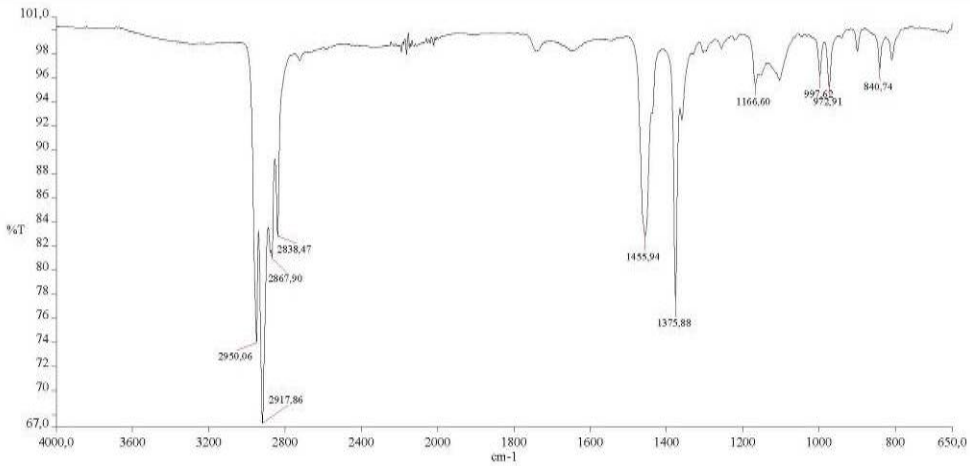


Fig. 4: FT-IR spectrum of PP (sample **192**).

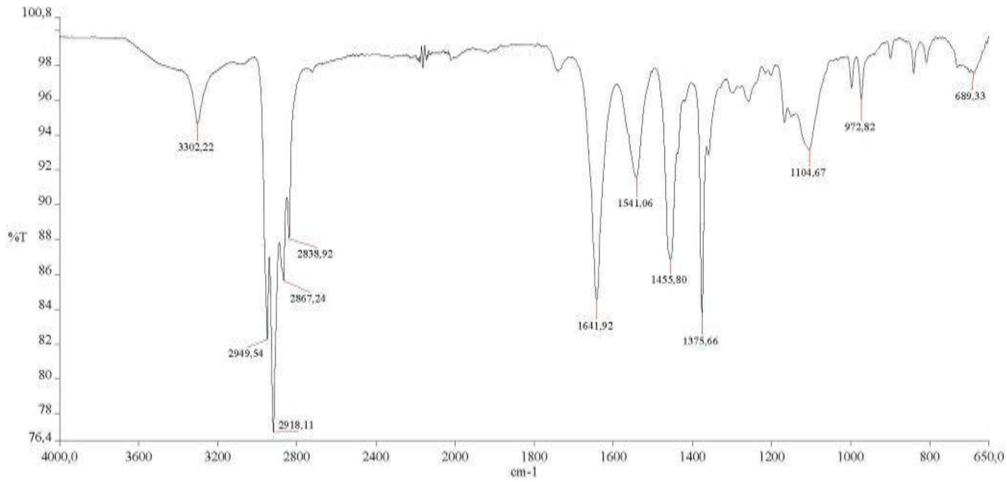


Fig 5: FT-IR spectrum of PAC 20 % (sample **197**).

Due to the chemical composition of the new fibre, PAC spectrum (Fig. 5) shows peaks attributed to its PA6 content (3302, 1641 and 1541 cm^{-1}), as well as peaks attributed to the PP matrix (1456 and 1376 cm^{-1}). The band at 3302 cm^{-1} can be attributed to N-H stretching vibration. The band at 1641 cm^{-1} corresponds to C=O vibrations of amide, whereas the bands at 1456 cm^{-1} and 1376 cm^{-1} can be attributed to asymmetric deformation vibration of CH_2 and bending vibration of CH_3, respectively.

A single spectrum is not sufficient to identify unequivocally the new fibre, because a similar spectrum would be obtained analysing a “physical mixture” of pure PP and PA6 fibres. To achieve the identification, two spectra are necessary: the first one on the sample as it is and the second one on the sample after dissolution of PA. In the case of PAC, subtracting the two spectra before and after dissolution of PA will result in a spectrum which still shows two small peaks (1542 and 1642 cm^{-1}), most probably related to the part of PA that is chemically linked to the microstructure of PAC through the compatibiliser (Figs. 6-7); vice versa, in the case of “physical mixture” PP – PA, the subtracted spectrum will just consist in the spectrum of pure PA (Fig. 8).

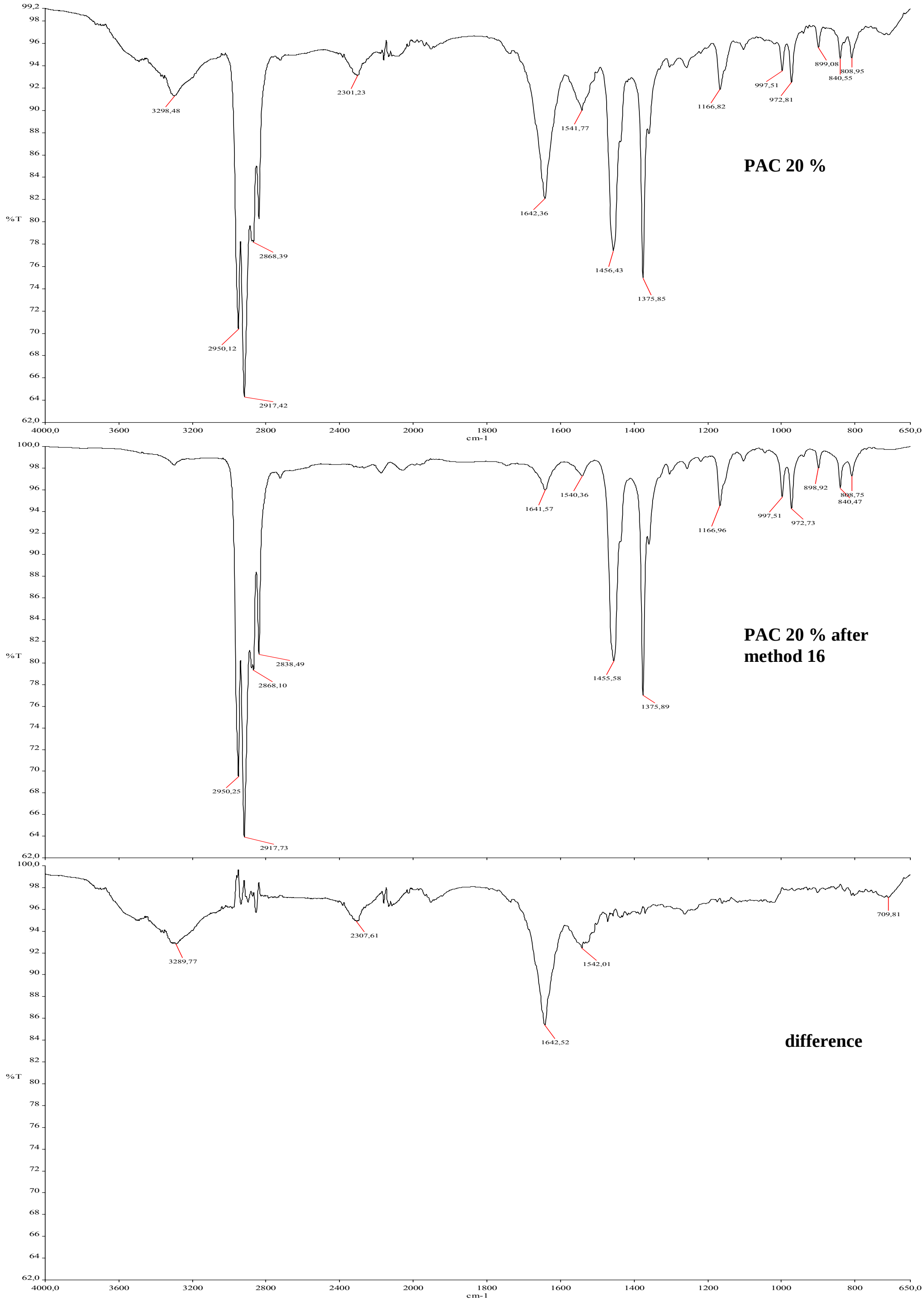


Fig. 6: FT-IR spectra of PAC 20 % (sample **197**) before and after method 16.

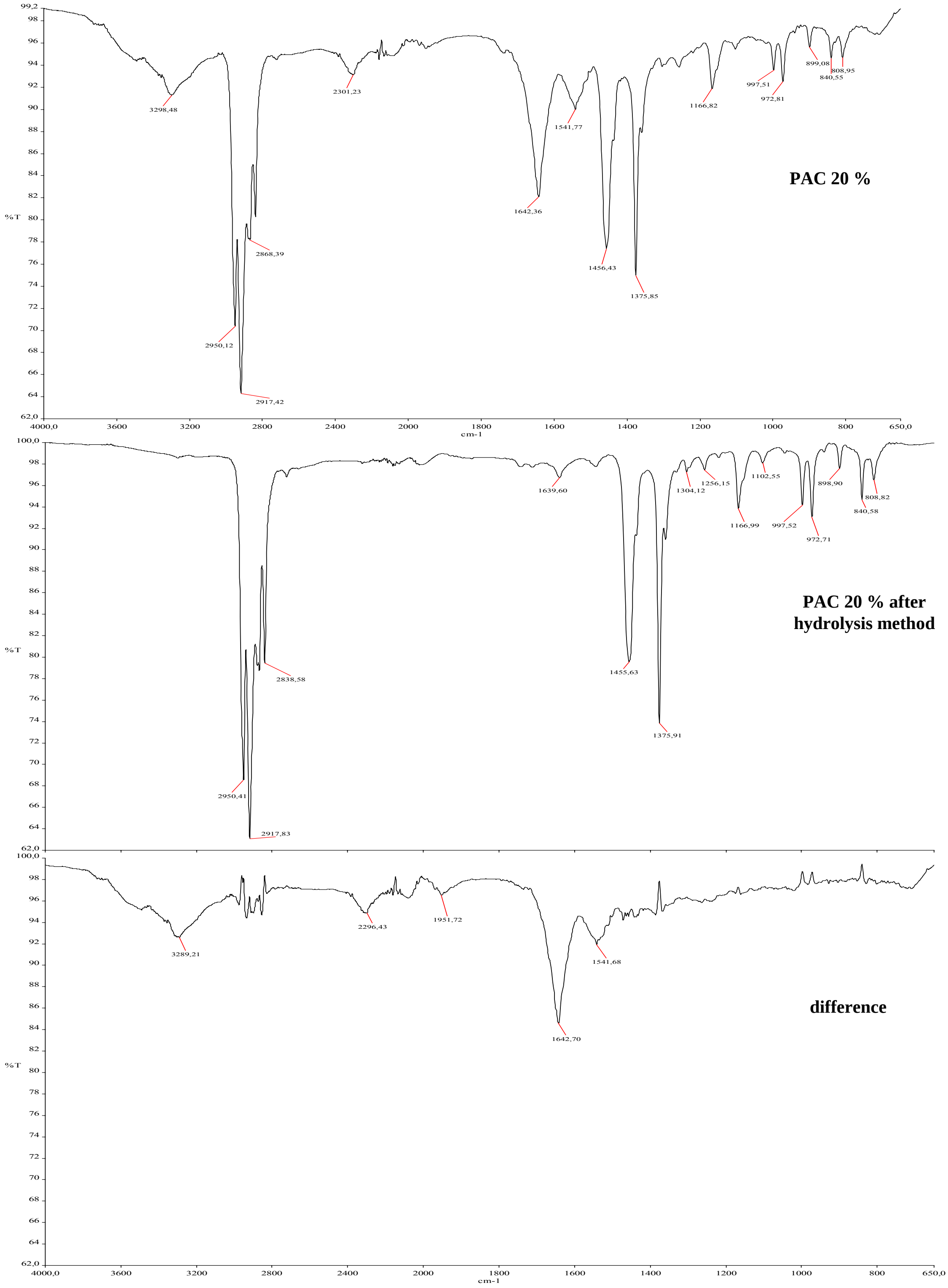


Fig. 7: FT-IR spectra of PAC 20 % (sample **197**) before and after hydrolysis method.

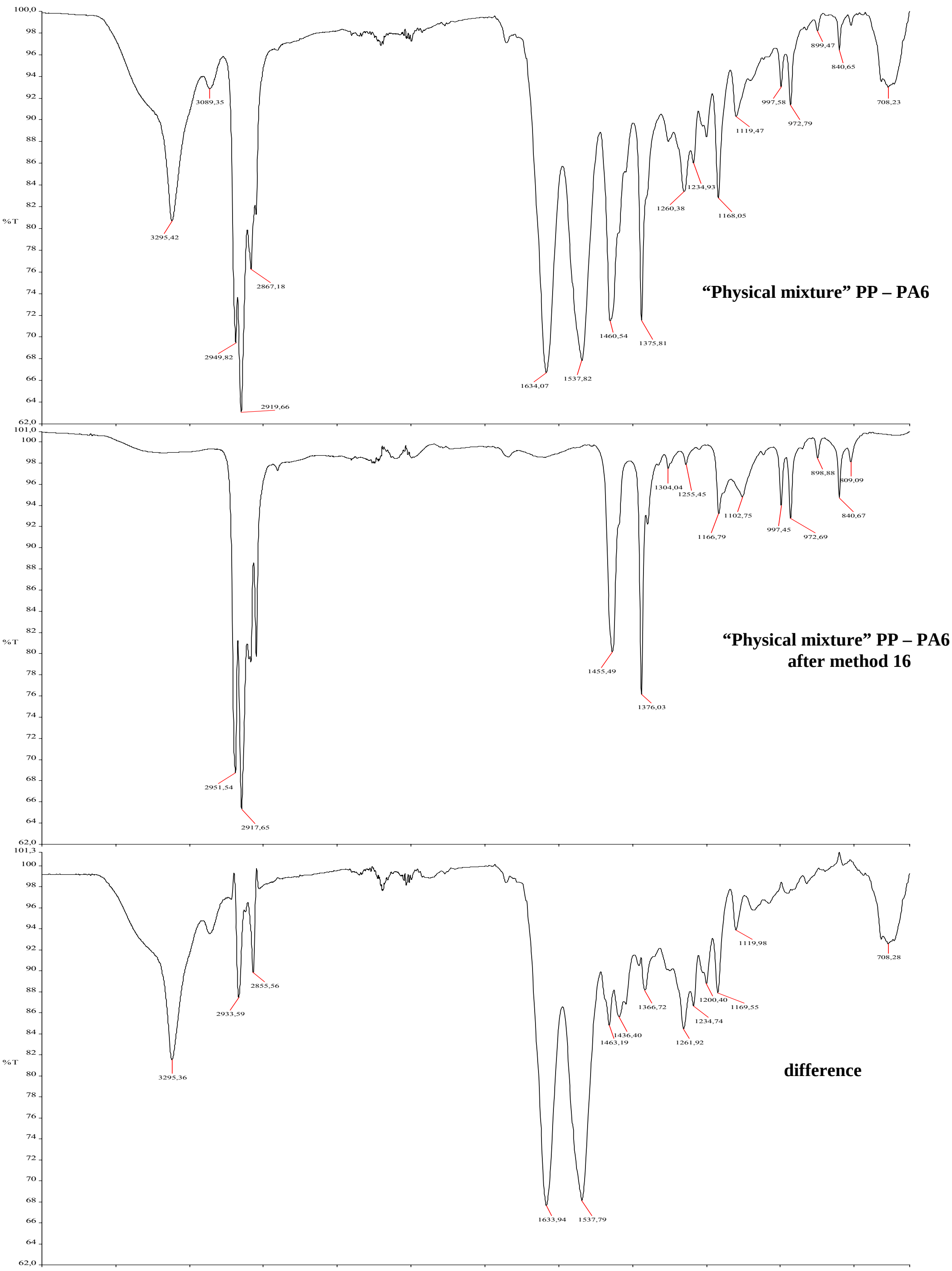


Fig. 8: FT-IR spectra of "physical mixture" PP – PA6 (PA6 content about 20 %) before and after method 16.

In particular, Fig. 6 shows the FT-IR spectra of PAC 20 %, before and after an acid attack, able to dissolve the PA6 fibrils. The method used was method 16 of Directive 96/73/EC, which treats the sample with 90 % formic acid solution in a water bath at 90 °C for 1 hour as contact time. Additionally, Fig. 7 reports the FT-IR spectra of PAC 20 %, before and after a different acid attack, using a method proposed by the petitioner for the quantification of the content of PA6 in PAC (hydrolysis method, see Annex I). The dissolution of PA6 is achieved by the use of a hydrochloric acid 18.5 % w/w aqueous solution at 75 ± 5 °C for 24 hours in a silicon bath.

In the case of a “physical mixture” PP – PA6 (containing 20 % PA6), the subtraction of spectra, before and after the application of method 16, shows a different result than in the case of PAC. Comparing the subtracted spectra reported in Figs. 6-7 with the one in Fig. 8, it can be clearly stated that the FT-IR technique is an efficient way to distinguish between PAC and “physical mixtures” of pure PP and PA fibres.

4.3 Differential scanning calorimetry

Differential Scanning Calorimetry (DSC) can also be used to identify PAC as a fibre, which is distinguishable from “physical mixtures” PP – PA6, as well as from binary mixtures PP/PAC and PA6/PAC. The equipment used for the analyses was a DSC model Q100 by TA Instruments. A temperature program of 10 °C/min, starting from 0 °C up to 260 °C, with a nitrogen gas flow of 50 ml/min was employed. The experimental method used consisted of a heating - cooling - heating cycle. Sample weight was in the range 6 - 10 mg. Fig. 9 shows the crystallisation and melting peaks of pure PP and PA6.

The crystallisation peaks of pure PP and PA6 are observed at 118 °C and 189 °C respectively, whereas their melting peaks (second heating) are found at 163 °C and 221 °C respectively. In Fig. 10, the DSC analyses of pure PAC 40 % and a “physical mixture” of PP – PA6 (containing 40.4 % PA6) can be compared.

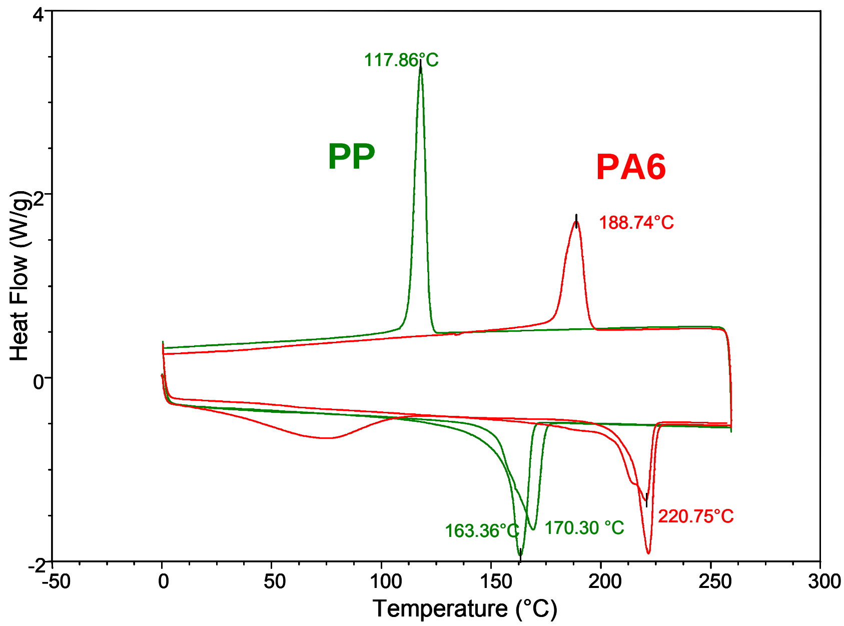


Fig. 9: DSC analysis of PP (sample **192**) and PA6 (sample **193**).

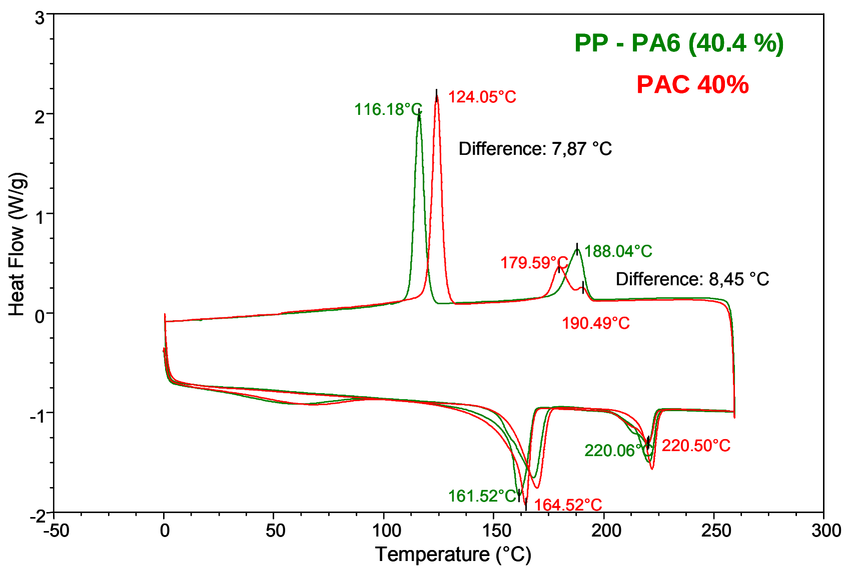


Fig. 10: DSC analysis of PAC 40 % (sample **199**) and a "physical mixture" PP - PA6 (40.4 %).

Observing the cooling cycle for the "physical mixture" PP - PA6, the crystallisation peak for PA6 was measured at 188 °C, as in the analysis of pure PA6. On the contrary, the crystallisation peak due to the PA6 fibrils in pure PAC was split in two: the first shoulder was measured at 190 °C (close to the one of pure PA6) and the second peak was recorded in the range of 180 °C, showing the tendency of moving towards the crystallisation peak of pure PP. Analogously, the crystallisation peak of PP in the physical mixture PP - PA6 was observed at about 116 °C (similar to the analysis of pure PP), whereas the crystallisation peak of PP in pure PAC (around

124 °C) was shifted towards the crystallisation peak of pure PA6. The differences in temperature for crystallisation peaks of PA6 and PP in the "physical mixture" and in the new fibre were about 8 °C.

Based on these data, it can be concluded that PAC is not a "physical mixture" of PP and PA6, as in the new fibre the crystallisation peaks of PA6 and PP move towards each other, possibly due to the formation of copolymers.

As shown in Fig. 11, the content of PA6 in PAC has an influence on the temperature of the crystallisation peak of PP. In fact, the lower the content of PA6 in PAC the smaller the difference between the temperature of PP crystallisation peak in PAC and the one of the crystallisation peak of pure PP. This phenomenon is coherent with the fact that PAC is more similar to pure PP when the content of PA6 decreases.

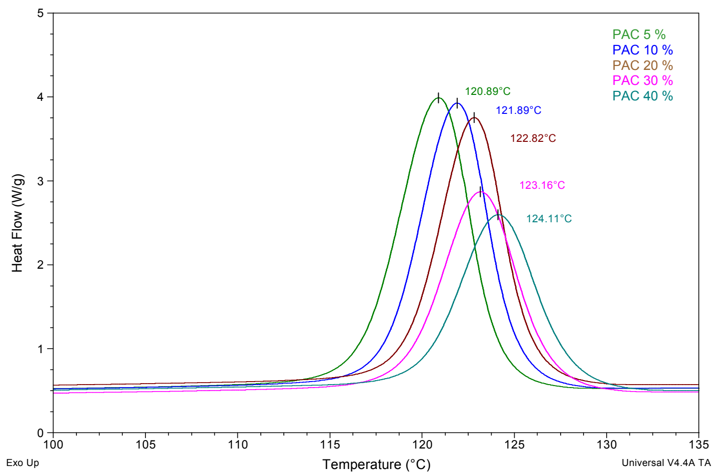


Fig. 11: Influence of PA6 content in pure PAC on PP crystallisation peak.

In Fig. 12, the cooling cycle for PAC 40 %, binary mixtures PP/PAC 40 % and PA6/PAC 40 % can be compared. In the region of the PA6 crystallisation peak of the sample made by PA6/PAC 40 %, a major peak (187 °C) and a secondary one (176 °C) can be observed. The first peak is probably due to the PA6 fibres in the mixture and to the "free" part of PA6 in PAC; the second one is most likely due to the part of PA6 embedded in PAC, which possibly formed copolymers with PP through the compatibiliser. Analogously, in the binary mixture PP/PAC 40%, two peaks can be seen in the PP peak region, one at 117 °C, due to the "free" PP fibres and another one at 124 °C, due to the PP content of PAC. Therefore, PAC and binary mixtures of PA6/PAC and PP/PAC can be clearly differentiated through DSC analysis.

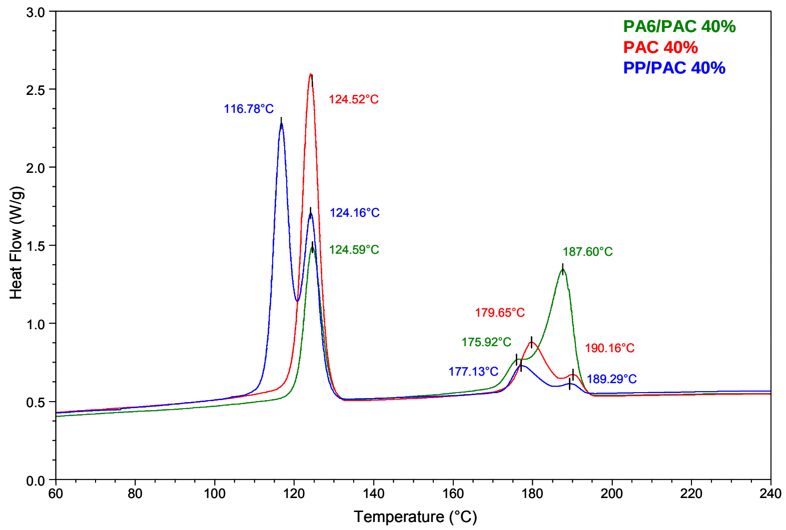


Fig. 12: DSC crystallisation cycle for PAC 40 % (sample **199**), a binary mixture PA6/PAC 40 % (sample **206**) and PP/PAC 40 % (sample **213**).

5. Test methods for quantification of the new fibre

Initially, the JRC verified the applicability of the usual pre-treatment to the new fibre and determined both the mass loss due to pre-treatment and the *agreed allowance*. Secondly, the behaviour of the new fibre was studied with all the methods described in Directive 96/73/EC. The behaviour of pure PA6 and pure PP was studied as well, in order to verify which methods were able to differentiate them. Thirdly, the methods proposed by the applicant (see Annex I) for the quantification of PA6 in PAC were evaluated together with other possible less time-consuming methods. Finally, all the samples made by binary mixtures received from Aquafil (**200** – **213**) were analysed by manual separation, chemical analysis and DSC analysis. Based on the evaluation of results on binary mixtures, methods 11 and 16 of Directive 96/73/EC were considered accurate enough to be tested with carpet samples (samples **234** – **257**). These carpet samples were also analysed *via* manual separation in order to have the reference values needed to evaluate the accuracy of the aforementioned chemical methods for quantification purposes.

Detailed results regarding mass loss due to pre-treatment, *agreed allowance*, solubility properties, manual separation and chemical methods are reported in Annex V.

5.1 Influence of drying conditions on PAC

The petitioner suggested that drying steps should always be conducted in vacuum oven (~ 40 mbar) in order to avoid degradation of PAC (in particular the polyamide part). Based on Aquafil's experiments, PAC seemed to be damaged when dried in a ventilated oven at 105 °C for longer than 6 h, probably due to thermo-oxidative processes. At the beginning of the experimental work, the JRC studied the influence of the use of ventilated oven during the drying step. Tests were performed on sample **160** (PAC 20 %), the only yarn sample of PAC available at that time. From a total of twelve replicates, weighed under repeatability conditions, six of them were dried in a vacuum oven and six in a ventilated one for 2, 4, 6, 8, 12 and 16 hours. The percentage of mass loss during the drying step is shown in Fig. 13. Although the mass loss remained constant during 16 hours when vacuum oven was used, a decrease of around 50 % was observed after 6 h, when ventilated oven was employed. This fact could be attributed to an oxidation of the new fibre, which could result in an increase of its weight and a decrease of mass loss. After 12 hours in the ventilated oven, the mass loss almost returned to its initial value, possibly due to a loss of volatile compounds from the oxidised sample. Moreover, using ventilated oven, the longer the drying step of samples the more serious the observed damages to the fibre. The fibre changed colour over the time from white to yellow (Fig. 14) and became more and more fragile. After 12 hours, the fibre could be disintegrated into dust when touched. Based on these experiments, a major part of the subsequent investigations were conducted drying samples in vacuum oven.

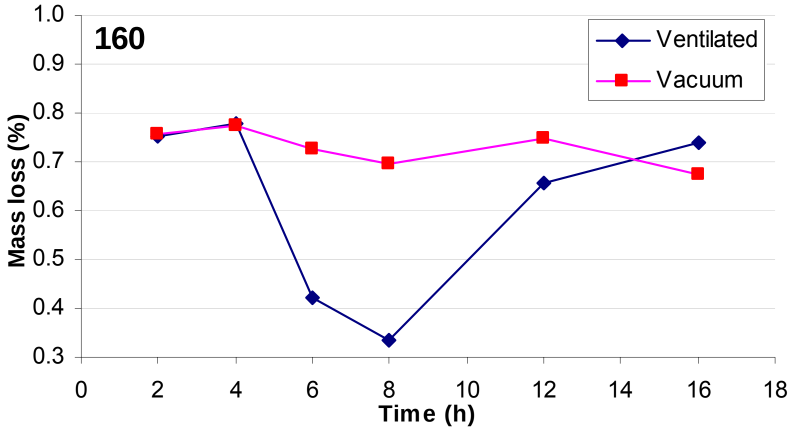


Fig. 13: Mass loss of sample **160** (PAC 20 %) dried in a vacuum or ventilated oven.

2 hours **4 hours** **6 hours** **8 hours** **12 hours** **16 hours**

Fig. 14: Gradual change in colour of sample **160** (PAC 20 %) when dried in a ventilated oven.

Vacuum oven is not foreseen in any of the methods in Directive 96/73/EC and costs more than a conventional ventilated one. For this reason, when more samples were sent by Aquafil later on, the influence of drying conditions was checked again on samples **197** and **233**, which have the same composition as sample **160** (PAC 20 %). Surprisingly, no differences in mass loss were recorded independently of the type of drying conditions used (vacuum *vs.* ventilated) (Figs. 15-16). Mass loss values were in the same range (0.7 - 0.8 %) for both samples.

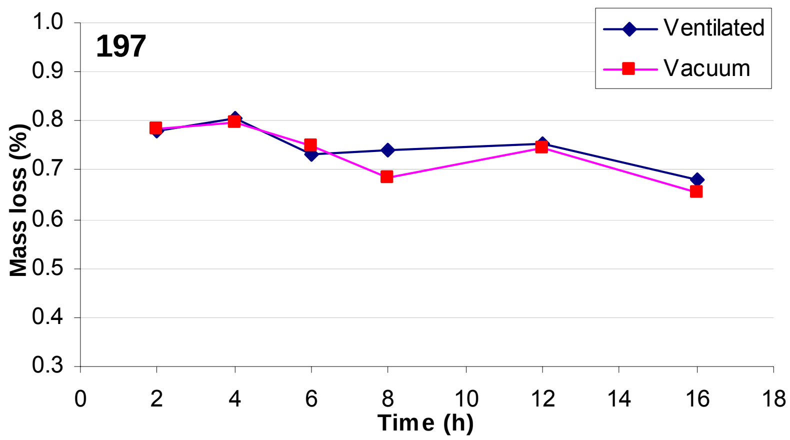


Fig. 15: Mass loss (%) of sample **197** (PAC 20 %) when dried in vacuum and ventilated oven.

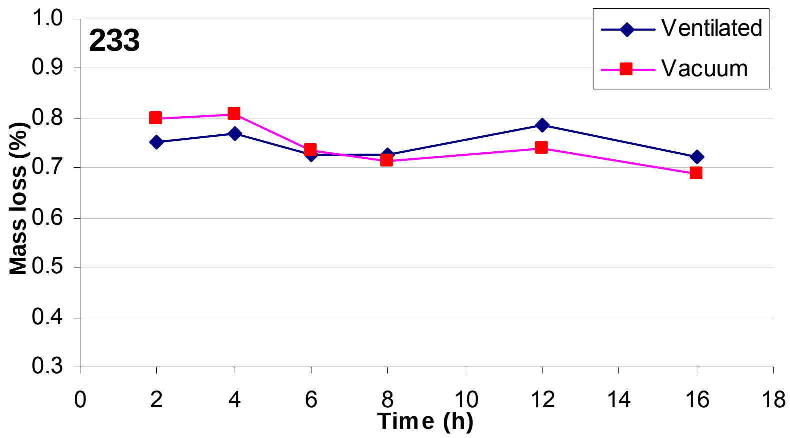


Fig. 16: Mass loss (%) of sample **233** (PAC 20 %) when dried in vacuum and ventilated oven.

In the case of vacuum oven, results were also comparable to the ones observed for sample **160**, whereas in the case of ventilated oven they were completely different. Samples **197** and **233** did not change to yellow even after 12 h in ventilated oven and, what is more important, these samples did not become fragile after the drying step in air (Figs. 17-18).

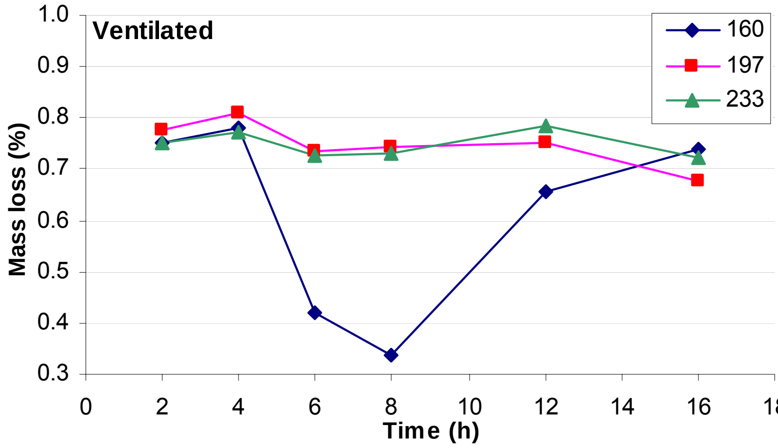


Fig. 17: Comparison of mass loss (%) of samples **160**, **197** and **233** (PAC 20 %) when dried in ventilated oven.

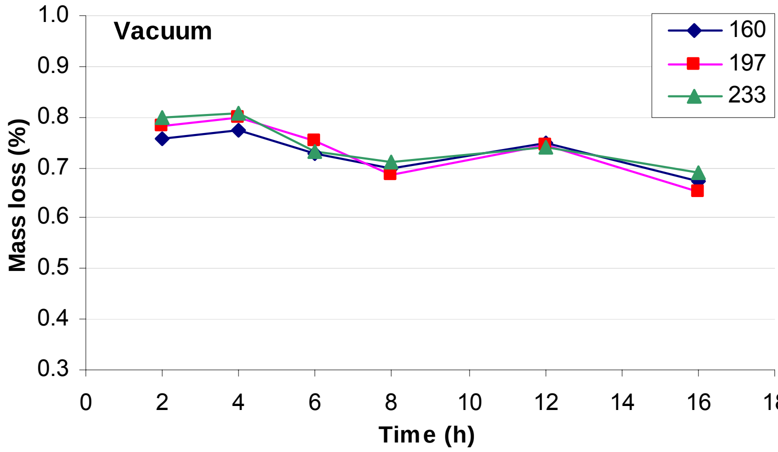


Fig. 18: Comparison of mass loss (%) of samples **160**, **197** and **233** (PAC 20 %) when dried in vacuum oven.

The JRC contacted immediately the company requesting information about possible differences in the production of samples **160**, **197** and **233**. Towards the end of the experimental investigation Aquafil confirmed that sample **160** was the only one showing degradation effect in ventilated oven. They communicated that sample **160** was very old and attributed its poor resistance to the inappropriate storage conditions under which it was kept before being sent to the JRC.

In conclusion, it was verified that ventilated oven can be safely applied since it does not cause any damage to the fibre. A further confirmation, that vacuum and ventilated oven give equivalent results, was obtained when the solubility properties of the new fibre and the correction factors *d* were evaluated. In that case, samples with nominal content of PA6 equal to 20 and 40 % were analysed and results were statistically compared (see par. 5.4.1).

5.2 Pre-treatment

Before quantification, samples should be pre-treated in order to eliminate non-fibrous matter. Directive 96/73/EC suggests extracting non-fibrous matter with light petroleum ether and water. The procedure foresees one-hour extraction in Soxhlet with light petroleum ether (boiling range 40 - 60 °C), followed by one-hour extraction in water at room temperature and one-hour extraction in water at 65 ± 5 ºC, using a liquor/specimen ratio of 100/1. An automatic hot-extractor (Soxhtec) instead of traditional Soxhlet was mostly employed for the pre-treatment, as no differences in terms of mass loss were noticed during the conduction of preliminary experiments.

In order to evaluate the *b* coefficient for the new fibre (mass loss due to pre-treatment), three consecutive complete pre-treatments were carried out on five replicates, five grams each, of PAC 20 %. Results (Table 3) showed a mass loss of 0.95 ± 0.03 % during the first pre-treatment, value in line with the content of finishing agents declared by Aquafil (1.00 ± 0.25 %). The second and third ones did not reveal any further significant mass loss. These evidences confirm that the new fibre is insoluble under the conditions of the pre-treatment. Therefore, in agreement with experts from member states, the usual pre-treatment was considered applicable and the *b* coefficient value for PAC was established to be 0 %.

Table 3: Mass loss due to pre-treatment.

JRC code	1st pre-treatment		2nd pre-treatment		3rd pre-treatment	
	loss of mass %	conf. limit (95 %)	loss of mass %	conf. limit (95 %)	loss of mass %	conf. limit (95 %)
233	0.95	0.03	0.15	0.01	0.12	0.02

Results on samples of PAC with various content of PA6 showed mass loss in the same range with an average value of 1 % (Table 4).

Table 4: Mass loss of PAC, PP and PA6 due to pre-treatment.

JRC code	composition	nominal PA6 %	replicates	mass loss %	conf. limit (95 %)
192	100 % PP	---	5	**1.09**	0.03
193	100 % PA6	---	5	**1.04**	0.11
195	100 % PAC	5	5	**1.09**	0.04
196	100 % PAC	10	5	**1.05**	0.03
197	100 % PAC	20	5	**1.06**	0.04
198	100 % PAC	30	4	**1.07**	0.04
199	100 % PAC	40	5	**0.94**	0.03
		average (PAC)		**1.04**	

Fig. 19 shows the comparison of FTIR spectra of PAC 40 % (sample **199**) as received and after pre-treatment.

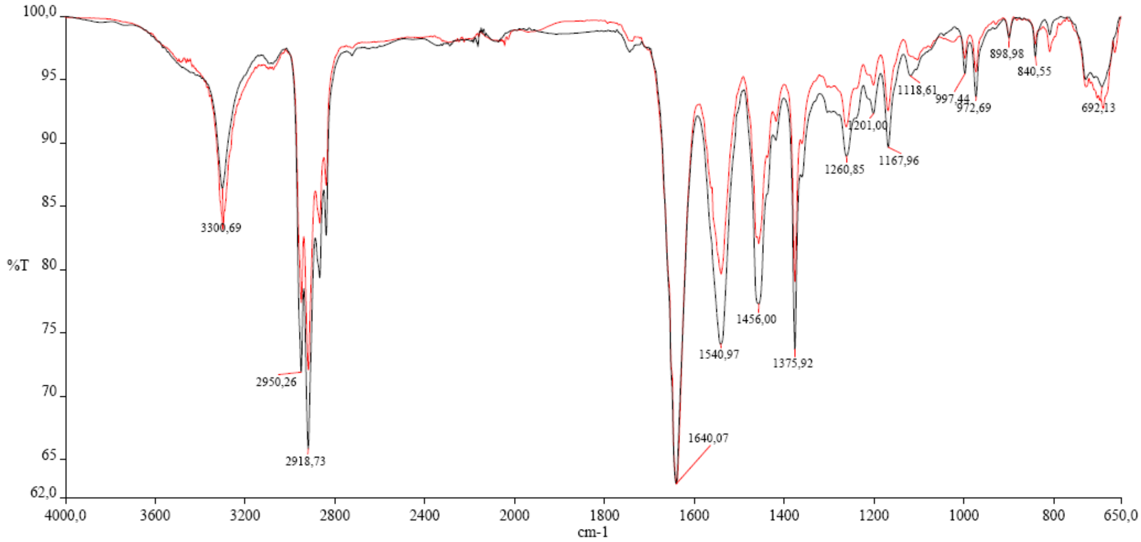


Fig. 19: Comparison of FT-IR spectra of untreated (---) and pre-treated (---) PAC 40 % (sample **199**).

5.3 Agreed allowance

The *agreed allowance* was considered equal to the moisture regain in standard atmosphere according to the definition stated in ISO 6348:1980 [4].

A number of experiments were performed on samples of PAC with different PA6 content (**195** – **199**), in order to evaluate the *agreed allowance* of the new fibre. This parameter was calculated both for untreated and pre-treated samples. The procedure described in the following was applied. Weighing bottles were dried for 5 h at 105 °C, then cooled in a dessicator and weighed. A sample of about 2 g of PAC was placed in each weighing bottle and dried for 16 h at 105 °C, then cooled in a dessicator and weighed. Samples were then conditioned for 72 hours at 20 ± 1 °C and 65 ± 2 % relative humidity and weighed immediately after the conditioning period. The following formulas were used to calculate the *agreed allowance*:

$$\text{water mass} = \text{wet sample mass} - \text{dried sample mass} \qquad 5.3.1$$

$$\textit{agreed allowance} = 100\ (\text{water mass} / \text{dried sample mass}) \qquad 5.3.2$$

Ten replicates per each sample were analysed (Table 5). Results were similar for untreated and pre-treated samples, showing a tendency to increase with the increase of PA6 content (Fig. 20). This fact can be justified by the larger moisture regain in standard atmosphere of the PA component compared to the PP one. Results showed values in the range of 0.09 - 1.15 %, depending on PA6 content, the average being 0.6 %.

Table 5: *Agreed allowance* (AA) for PAC.

JRC code	composition	replicates	untreated sample AA %	untreated sample conf. limit (95%)	pre-treated sample AA %	pre-treated sample conf. limit (95%)
195	PAC 5 %	10	**0.15**	0.01	**0.09**	0.03
196	PAC 10 %	10	**0.29**	0.01	**0.22**	0.05
197	PAC 20 %	10	**0.56**	0.02	**0.52**	0.04
198	PAC 30 %	10	**0.88**	0.03	**0.79**	0.06
199	PAC 40 %	10	**1.15**	0.03	**1.14**	0.03
		average	**0.61**		**0.55**	
		overall average		**0.58**		

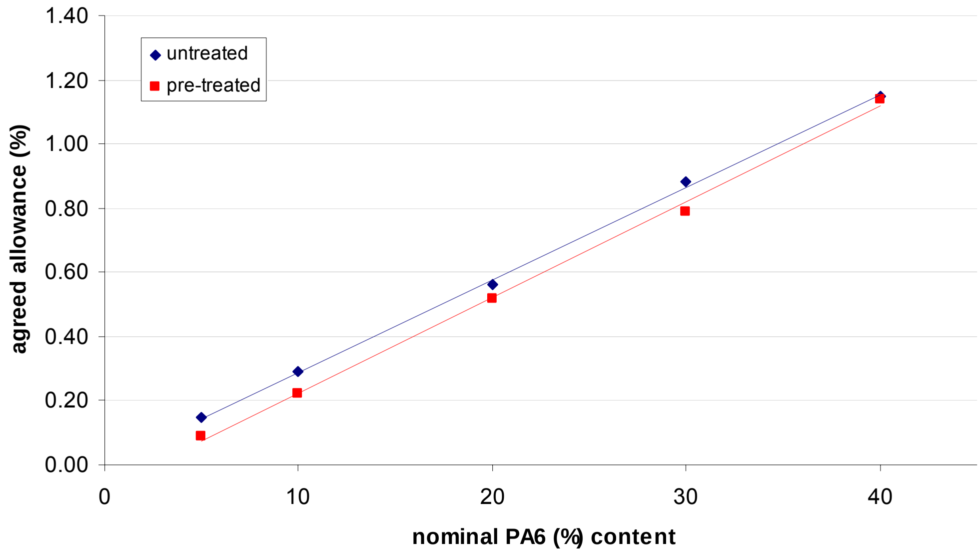


Fig. 20: *Agreed allowance* values for pre-treated and untreated samples of PAC *vs*. % PA6 content.

Based on experimental results and after discussions with experts from member states, even though the value proposed by Aquafil was 1.6 %, it was agreed to establish a value of 1.00 % for the *agreed allowance* of PAC.

5.4 Solubility properties

The solubility properties of PP, PA6 and the new fibre were studied and correction factors d for mass loss of the insoluble component in the reagents during analysis were evaluated. The correction factors d were calculated using the following formula:

$$d = \frac{m}{r} \qquad 5.4.1$$

where:

m is the dry mass of the specimen after pre-treatment

r is the dry mass of the residue

All weighing operations were performed using an analytical balance of weighing capacity of 0.01 mg. The percentages of insoluble component on a clean, dry mass basis, disregarding loss of fibre mass during pre-treatment, were calculated using the following formula:

$$P_1\% = \frac{100\ r\ d}{m} \qquad 5.4.2$$

where:

P_1 is the percentage of clean, dry insoluble component

m is the dry mass of the specimen after pre-treatment

r is the dry mass of the residue

d is the correction factor for loss of mass of the insoluble component in the reagent during analysis

In the case of binary mixtures, calculations of percentage of insoluble component on clean, dry mass basis, with adjustment by conventional factors (*agreed allowances*) and, where appropriate, correction factors b for loss of mass during pre-treatment, were performed using the following formula:

$$P_{1A}\ \% = \frac{100\ P_1 \left(1 + \frac{a_1 + b_1}{100}\right)}{P_1 \left(1 + \frac{a_1 + b_1}{100}\right) + (100 - P_1)\left(1 + \frac{a_2 + b_2}{100}\right)} \qquad 5.4.3$$

where:

P_{1A} is the percentage of insoluble component, adjusted by *agreed allowances* and for loss of mass during pre-treatment

P_1 is the percentage of clean, dry insoluble component as calculated from equation 5.4.2

a_1 is the *agreed allowance* for the insoluble component (listed in Annex V to the Directive 2008/121/EC on textile names)

a_2 is the *agreed allowance* for the soluble component (listed in Annex V to the Directive 2008/121/EC on textile names)

b_1 is the percentage loss of insoluble component caused by the pre-treatment

b_2 is the percentage loss of soluble component caused by the pre-treatment

The percentage of the soluble component (P_{2A} %) was obtained by difference.

The coefficients b used in the calculations were: 1 % for PP, 0 % for PA6 (as pointed out in Directive 96/73/EC) and 0 % for PAC. The *agreed allowances* used in the calculations were: 1.00 % for PAC, 2.00 % for PP and 6.25 % (in case of discontinuous fibre) or 5.75 % (in case of filament) for PA6.

The solubility properties of PP and PA were studied in the case that they were not known from Directive 96/73/EC, with the aim to find methods which could differentiate PP from PA in order to try to dissolve only one of the two polymers in PAC. In addition, pre-treated specimens of about 1 g of PAC were analysed with all the chemical methods (apart from method 12 for nitrogen content) described in Directive 96/73/EC.

For each sample 10 - 20 replicates were analysed. The data were collected and subjected to statistical evaluation. The results were first examined for evidence of outliers using Grubbs' statistical test, as laid down in ISO 5725 [5]. Only few outliers were found out of all measurements and they were eliminated. The valid results were then subjected to a further statistical evaluation. The average and standard deviation (SD) of each set of data were calculated, as well as the relative standard deviation (RSD). The RSD was used to measure the dispersion of the distribution of test results in one laboratory: the lower the value of RSD, the better the repeatability of the method. The confidence intervals were calculated at 95 % probability, using the following formula:

$$\mu = x_m \pm \frac{t\ s}{\sqrt{n}} \qquad 5.4.4$$

where:

t	is the value listed in the Student's *t*-distribution for a certain number of degrees of freedom and level of probability
s	is the estimated standard deviation
μ	is the true value
x_m	is the average of experimental results
n	is the number of measurements

Annex V reports all results regarding the evaluation of correction factors *d* and the composition analyses. An overview of results regarding the solubility properties of PP, PA6 and PAC is shown in the following tables. Table 6 shows the solubility properties of PP, whereas Table 7 shows the ones of PA for the quantitative methods of Directive 96/73/EC. Only the methods in which PP and/or PA were not included in the field of application were tested.

Table 6: Solubility properties of PP.

JRC code	method	replicates	PP %	conf. limit (95%)	*d*	conf. limit (95%)
186-187-192	1	20	99.75	0.04	1.003	0.0004
192	3	20	99.90	0.04	1.001	0.0005
192	5	19	99.87	0.05	1.001	0.0005
186-187-192	6	20	99.78	0.06	1.002	0.001
192	7	20	100.19	0.18	0.998	0.002
192	8	20	99.92	0.03	1.001	0.0004
192	9	20	99.64	0.07	1.004	0.001
192	10	20	99.86	0.05	1.001	0.001
192	11	20	100.01	0.09	1.000	0.001
192	14	18	100.01	0.12	1.000	0.001
113	15	10	100.00	0.03	soluble	-
192	16	20	99.77	0.04	1.002	0.0004

Table 7: Solubility properties of PA6.

JRC code	method	replicates	PA6 %	conf. limit (95%)	*d*	conf. limit (95%)
193	3	10	99.88	0.04	soluble	-
193	5	10	99.76	0.07	1.003	0.001
193	7	10	99.87	0.04	soluble	-
193	10	10	98.91	0.06	1.012	0.001
193	11	10	99.88	0.01	soluble	-
193	16	10	99.93	0.02	soluble	-

Results showed that PP is insoluble in all the tested methods (d = 1.00), apart from method 15 (cyclohexanone) which solubilised completely this fibre. On the contrary, PA6 is soluble in methods 3, 7, 11 and 16, whereas it is insoluble in methods 5 and 10 (d = 1.00 and 1.01 respectively).

The solubility properties of PA6 and PP are compared in Table 8. Methods 3, 4, 7, 11, 13, 14, 15 and 16 were shown to be able to differentiate among PP and PA. Therefore, these methods were further taken into consideration in order to verify if they could be used to quantify PA6 in PAC. It has to be noted that no solvent used in the methods of Directive 96/73/EC can dissolve both PP and PA.

Table 8: Comparison of solubility properties of PP and PA6.

method	PP *d* factor	PA6 *d* factor
1	1.00	1.00
2	1.00	1.00
3	1.00	soluble
4	1.00	soluble
5	1.00	1.00
6	1.00	1.00
7	1.00	soluble
8	1.00	1.00
9	1.00	1.00
10	1.00	1.01
11	1.00	soluble
13	soluble	1.00
14	1.00	soluble
15	soluble	1.00
16	1.00	soluble

At first, the solubility properties of the new fibre were evaluated on PAC 40 % (sample **199**), using vacuum oven due to the difficulties mentioned in par. 5.1. The intention was to start considering the sample with the highest probability to be partially dissolved, in the case solubility properties would depend on the content of PA6 in PAC. An overview of results is shown in Table 9.

Table 9: Solubility properties of PAC 40 % (sample **199**).

JRC code	method	replicates	insoluble comp. %	conf.limit (95%)	*d*	conf.limit (95%)
199	1	10	99.54	0.10	1.005	0.001
199	2	10	100.07	0.07	0.999	0.001
199	3	9	65.85	0.33	partially soluble	-
199	4	14	66.98	0.15	partially soluble	-
199	5	10	100.02	0.03	1.000	0.0003
199	6	10	99.65	0.05	1.004	0.0005
199	7	10	68.57	0.21	partially soluble	-
199	8	19	99.86	0.57	1.002	0.006
199	9	9	99.56	0.13	1.004	0.001
199	10	10	99.91	0.04	1.001	0.0004
199	11	9	97.82	0.04	1.023	0.0004
199	13	8	40.22	0.23	partially soluble	-
199	14	8	66.60	0.18	partially soluble	-
199	15	9	40.35	1.38	partially soluble	-
199	16	25	64.82	0.10	partially soluble	-

PAC 40 % was proved to be insoluble in methods 1, 2, 5, 6, 8-11. The *d* values observed were 1.00 for methods 1, 2, 5, 6, 8-10 and 1.02 for method 11. On the contrary, PAC 40 % was partially soluble using methods 3, 4, 7, and 13-16.

Interestingly, comparing results in Tables 7 and 9, it appears evident that even if polyamide is soluble in method 11, the PA component of PAC is not. This is probably due to the inert shield of the polypropylene matrix and to the difficulty of the reagent to penetrate the fibre structure.

In order to verify the possible influence of the content of PA6 in PAC on its solubility properties, some of the methods were also applied to sample **233** (PAC 20 %). All methods where PAC 40 % was insoluble (1, 2, 5, 6, 8-11), as well as selected methods where the same sample was partially soluble (14 and 16), were tested. An overview of results is shown in Table 10.

Table 10: Solubility properties of PAC 20 % (sample **233**).

JRC code	method	replicates	insoluble comp. %	conf. limit (95%)	*d*	conf. limit (95%)
233	1	5	100.26	0.56	0.997	0.006
233	2	5	99.99	0.21	1.000	0.002
233	5	5	100.47	0.58	0.995	0.006
233	6	5	100.00	0.28	1.000	0.003
233	8	5	99.95	0.15	1.001	0.001
233	9	5	99.92	0.20	1.001	0.002
233	10	5	100.17	0.27	0.998	0.003
233	11	5	99.60	0.06	1.004	0.001
233	14	5	99.40	0.06	1.006	0.001
233	16	5	81.17	0.17	partially soluble	-

Table 11: Comparison of *d* correction factors of PAC 20 % (sample **233**) and PAC 40 % (sample **199**).

Method	*d* factor	
	233 (20 %)	199 (40 %)
1	1.00	1.00
2	1.00	1.00
5	1.00	1.00
6	1.00	1.00
8	1.00	1.00
9	1.00	1.00
10	1.00	1.00
11	1.00	1.02
14	1.01	partially soluble
16	partially soluble	partially soluble

A comparison of the *d* correction factors for the methods tested with the two PAC samples of different PA6 content is shown in Table 11. The content of PA6 greatly influenced the solubility properties of PAC when method 14 was applied; although PAC 40 % (sample **199**) was partially soluble in this method, PAC 20 % (sample **233**) was proved to be insoluble. On the contrary, the content of PA6 in PAC did not at all affect the solubility properties of the new fibre when methods 1, 2, 5, 6, 8, 9 and 10 were applied; PAC samples **233** and **199** presented the same *d* correction factors for these methods (1.00 in all cases). Regarding method 16, the solubility of PAC was much greater in the case of sample **199** (Tabs. 9-10) than in the case of sample **233**, fact that could be easily attributed to the higher content of the soluble component (PA6) in these specimens. In the case of method 11, a difference of 0.2 % was observed between PAC 20 % and 40 % (*d* factors 1.00 and 1.02 respectively).

Since the *d* correction factor for method 11 depended on PA6 content, its value was evaluated in the range of PAC's composition available (10 – 40 %), which covered the range in the definition initially proposed (10 – 45 %). As expected, the correction factor *d* for method 11 slightly increased with PA6 content, the average value being 1.01 (Table 12).

Table 12: Correction factors *d* for PAC (method 11).

JRC code	nominal PA6 %	n	PAC %	conf. limit (95 %)	*d*	conf. limit (95 %)
195	5	10	99.86	0.03	**1.001**	0.0003
196	10	10	99.63	0.12	**1.004**	0.0013
197	20	10	99.48	0.14	**1.005**	0.0014
198	30	10	99.03	0.05	**1.010**	0.0005
199	40	9	97.82	0.04	**1.023**	0.0004
				average (196 - 199) :	**1.010**	

5.4.1 Influence of drying conditions on solubility properties of PAC

A further confirmation that a ventilated oven can be used, instead of a vacuum one, without damaging the fibre was obtained comparing results regarding the solubility properties of PAC in a variety of methods. The sample selected for this study was sample **233** (PAC 20 %), as it was in production at the time of the study. All methods of Directive 96/73/EC where both PAC 40 % and 20 % (samples **199** and **233**) were proved to be insoluble were tested. The influence of drying conditions was also studied in the case of method 16, as this method could be used for quantification purposes, such as PA6 content in PAC (see par. 5.5.5). Method 14, where only sample **233** was insoluble, was investigated as well.

For each tested method ten replicates were analysed, with the drying conditions as fixed parameter; five of them were dried in a ventilated oven and the other five in a

vacuum one. The null hypothesis was that the two methods would give the same result (i.e., the difference between the two averages could be attributed to random errors).
First of all, the standard deviations of the two independent sets of measurements (s_1 and s_2, with the number of replicates $n_1 = n_2 = 5$) were analysed with the F-test (two-sided test) to determine if the two experimental procedures had standard deviations which differed significantly [6].
To check the variances, the statistic F was calculated:

$$F = \frac{s_1^2}{s_2^2} \qquad 5.4.1.1$$

where s_1^2 is the bigger variance, as F must be higher than 1.
Taking into consideration the degrees of freedom for each set of measurements (4 in both cases) and the confidence level required (95 % probability), F values were compared with the critical value $F_{4,4}$ (P=0.05) reported in tables. If F value was higher than F critical, it was assumed that there was a statistically significant difference between the two variances.
To judge if the averages of two independent sets of measurements differed significantly, in the case of non significant difference between variances, the statistic t was calculated as follows:

$$t = \frac{(\bar{x}_1 - \bar{x}_2)}{s\sqrt{\frac{1}{n_1} + \frac{1}{n_2}}} \qquad 5.4.1.2$$

where $\bar{x}_1$ and $\bar{x}_2$ are the sample means and n_1 and n_2 the number of replicates for the two sets of measurements. The degrees of freedom of t are $n_1 + n_2 - 2$.
The standard deviation was calculated with the following formula:

$$s^2 = \frac{(n_1 - 1)s_1^2 + (n_2 - 1)s_2^2}{(n_1 + n_2 - 2)} \qquad 5.4.1.3$$

If the difference between variances was significant, then the statistic t was calculated as follows:

$$t = \frac{(\bar{x}_1 - \bar{x}_2)}{\sqrt{\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}}} \qquad 5.4.1.4$$

with the degrees of freedom estimated using the Welch-Satterthwaiteu approximation:

$$\nu = \frac{\left(\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}\right)^2}{\left(\frac{s_1^4}{n_1^2(n_1-1)} + \frac{s_2^4}{n_2^2(n_1-1)}\right)} \qquad 5.4.1.5$$

When necessary, the calculated value of ν was rounded down to the nearest integer. Finally, t values were compared with the critical value t (P=0.05) reported in the Student's t-distribution tables. According to the t-test, the difference between the two averages could be considered not significant when the calculated $|t|$ value did not exceed the critical one.

The overview of results is shown in Tables 13 and 14. In all cases, the statistical analyses showed that results obtained with vacuum and ventilated oven could be considered equivalent at 95 % probability.

Table 13: Comparison of *d* factors obtained using vacuum *vs*. ventilated oven (sample **233**).

Method	Vacuum oven			Ventilated oven			*F*	*F crit*	SD	*t*	*t crit*	average
	d factor	SD	n	*d* factor	SD	n						
1	0.997	0.0045	5	1.003	0.0011	5	17.60	9.60	≠	2.762	2.776	=
2	1.000	0.0017	5	1.002	0.0012	4	2.13	15.10	=	1.990	2.365	=
5	0.995	0.0046	5	0.992	0.0063	5	1.84	9.60	=	0.958	2.306	=
6	1.000	0.0023	5	1.003	0.0002	5	93.91	9.60	≠	2.542	2.776	=
8	1.001	0.0012	5	1.001	0.0010	5	1.30	9.60	=	0.053	2.306	=
9	1.001	0.0016	5	1.003	0.0001	5	281.65	9.60	≠	2.618	2.776	=
10	0.998	0.0022	5	1.001	0.0018	5	1.43	9.60	=	2.220	2.306	=
11	1.004	0.0005	5	1.005	0.0004	5	1.97	9.60	=	2.195	2.306	=
14	1.006	0.0005	5	1.006	0.0034	5	41.23	9.60	≠	0.150	2.776	=

Table 14: Comparison of soluble component obtained using vacuum *vs.* ventilated oven (sample **233**).

Method	Vacuum oven			Ventilated oven			*F*	*F crit*	SD	*t*	*t crit*	average
	soluble comp. %	SD	n	soluble comp. %	SD	n						
16	18.828	0.1397	5	18.878	0.0083	5	283.43	9.60	≠	0.788	2.776	=

To verify that the drying conditions have no influence on the solubility properties of PAC, even in the case of higher PA6 content, a variety of methods were tested on sample **199** (PAC 40 %). A number of methods which partially solubilised PAC 40 % (4, 7 and 16), as well as some methods in which PAC 40 % was insoluble (10 and 11) were tested. Results were subjected to statistical evaluation and are presented in Tables 15 and 16.

Table 15: Comparison of soluble component obtained using vacuum *vs.* ventilated oven (sample **199**).

Method	Vacuum oven			Ventilated oven			*F*	*F* crit	SD	*t*	*t* crit	average
	soluble comp. %	SD	n	soluble comp. %	SD	n						
4	33.016	0.2613	14	33.173	0.1906	10	1.88	3.83	=	1.618	2.074	=
7	31.433	0.2932	10	31.501	0.3543	10	1.46	4.03	=	0.470	2.101	=
16	35.177	0.2409	25	35.259	0.0828	10	8.47	3.61	≠	1.500	2.035	=

Table 16: Comparison of *d* factors obtained using vacuum *vs*. ventilated oven (sample **199**).

Method	Vacuum oven			Ventilated oven			*F*	*F* crit	SD	*t*	*T* crit	average
	d factor	SD	n	*d* factor	SD	n						
10	1.001	0.0006	10	1.001	0.0009	4	2.37	5.08	=	1.352	2.179	=
11	1.023	0.0005	9	1.032	0.0016	10	10.19	4.36	≠	17.698	2.201	≠

Examining Tables 15 and 16 it can be concluded that, in the case of PAC 40 %, an influence of drying conditions was observed only applying method 11. The mass loss of PAC 40 % obtained using ventilated oven was slightly higher than the one evaluated using vacuum oven. Therefore, all available compositions of PAC were analysed with method 11, performing all the drying steps in a ventilated oven (Table 17). The aim was to obtain an average *d* factor value under these conditions in the range of interest (PAC 10 – 40 %) and to compare it with the one obtained in the case of vacuum oven (1.01).

Table 17: Correction factors *d* for PAC (method 11, ventilated oven).

JRC code	nominal PA6 %	n	PAC %	conf. limit (95 %)	*d*	conf. limit (95 %)
195	5	10	99.95	0.37	**1.001**	0.0037
196	10	10	100.34	0.33	**0.997**	0.0033
197	20	9	99.52	0.02	**1.005**	0.0003
198	30	10	99.27	0.09	**1.007**	0.0009
199	40	10	96.93	0.11	**1.032**	0.0011
			average (196 - 199) :		**1.010**	

Comparing Tables 12 and 17 it can be seen that the *d* factor, expressed with two decimals, changed only in the case of PAC 40 %, when ventilated oven was used instead of the vacuum one. However, it should be highlighted that, although the *d* value was increased from 1.02 to 1.03 for sample **199** when ventilated oven was used, the average *d* factor value remained constant (1.01). This fact proved an overall non-significant influence of the drying conditions on the solubility properties of PAC, also in the case of method 11.

5.5 Quantification of PA6 in PAC

Nowadays, the production of PAC is restricted to a percentage of PA6 around 20 %; however, since the definition proposed by Aquafil foresees a wide range of composition (10 – 45 %), a method to quantify the content of PA6 in PAC should be available.

The methods proposed by the petitioner for this purpose were three: the first one was based on hydrolysis, the second one on DSC analysis and the third one on FT-IR analysis (see Annex I). In addition, a series of chemical dissolution methods were investigated in the attempt to find alternative less time-consuming methods for this quantification.

The JRC examined the applicability and tried to evaluate the accuracy of all these methods. Elemental analysis was used with the intention to quantify PA6 in PAC on the basis of the nitrogen content of PAC samples, which is only due to the polyamide component. Results obtained with this method were considered reference values against which all other results were compared.

5.5.1 *Elemental analysis*

Due to the composition of the new fibre (polypropylene and polyamide, plus a nitrogen-free compatibiliser), elemental analysis was carried out to evaluate the per cent of nitrogen in the fibre and from this value the content of PA6 in PAC. Results were calculated based on the value of per cent nitrogen obtained for PA6 (sample **193**). The analyses were performed in duplicate at the University of Camerino, Department of Chemical Sciences, Camerino (MC), Italy.

The principle of elemental analysis is based on the burning of samples and on the evaluation of the elements' content. The fibre is completely burnt during the analysis, consequently both the polyamide linked through the compatibiliser to polypropylene and the "free" polyamide are taken into consideration.

This technique is generally considered accurate and usually provides reproducible results; for these reasons, the results obtained with this method were considered as reference values and used to evaluate the performance of the other proposed methods.

Table 18: Quantification of PA6 in PAC (elemental analysis).

JRC code	composition	nitrogen %	SD	PA6 %	difference *vs.* nominal
195	PAC 5 %	0.850	0.342	**7.11**	2.11
196	PAC 10 %	1.280	0.011	**10.72**	0.72
197	PAC 20 %	2.368	0.005	**19.83**	-0.17
233	PAC 20 %	2.371	0.004	**19.85**	-0.15
198	PAC 30 %	3.398	0.006	**28.45**	-1.55
199	PAC 40 %	4.368	0.001	**36.57**	-3.43
193	PA6 100 %	11.944	0.001		

As shown in Table 18, standard deviations were usually very low with the exception of sample **195**. The content of PA6 measured *via* elemental analysis was in good agreement with the nominal content in the case of samples **196**, **197** and **233** (10 %, 20 % and 20 % respectively), whereas differences in the range of 1-3.5 % were obtained in the rest of concentrations. It has to be highlighted, however, that the production process was optimised by Aquafil only for the actual production (PAC 20 %).

5.5.2 *Hydrolysis method*

Hydrolysis was proposed by the petitioner as a method to quantify PA6 inside the new fibre. The procedure foresees that 1 g of cut sample (dried for 16 h at 105 °C) is put in a round-bottom flask which contains an aqueous solution with hydrochloric acid 18.5 % w/w (100 ml/g of sample). The flask is connected to a condenser and placed in a silicon bath at 75 ± 5 ^{o}C. The reaction must be continued for 24 hours. In the end, the sample has to be filtered through a filter crucible (porosity 1) and washed with plenty of water until the washing liquor shows a neutral pH. The sample is then dried again (16 h at 105 °C) and weighed.

This method is meant to hydrolyse all the amidic bonds present in the polyamide component, both "free" and linked through the compatibiliser to the other component and is, therefore, supposed to give results comparable to the ones obtained with elemental analysis.

Table 19: Quantification of PA6 in pure PAC (hydrolysis method).

JRC code	nominal PA6 %	elemental analysis PA6 %	hydrolysis Aquafil PA6 %	hydrolysis (JRC)			difference *vs.* elemental analysis	difference *vs.* hydrolysis Aquafil
				PA6 %	conf. limit (95%)	replicates		
195	5	7.11	4.81	**3.24**	0.62	5	-3.87	-1.57
196	10	10.72	9.59	**7.97**	0.33	5	-2.75	-1.62
197	20	19.83	18.60	**18.25**	0.51	4	-1.58	-0.35
198	30	28.45	27.46	**25.65**	0.61	5	-2.80	-1.81
199	40	36.57	35.74	**36.05**	0.35	5	-0.52	0.31
233	20	19.85	not provided	**18.72**	0.31	4	-1.13	-

As shown in Table 19, results obtained with hydrolysis were not in good agreement with the reference values and were always much lower than them; differences ranged from 0.5 % to almost 4 % depending on the sample. JRC and Aquafil's results were similar only in the case of samples **197** and **199** (PA6 content 20 % and 40 % respectively). Consequently, the hydrolysis method was not considered accurate enough for the quantification of PA6 in PAC. In addition, the method was very time consuming and did not show high repeatability.

5.5.3 *DSC method*

DSC was proposed by the petitioner in order to quantify PA6 inside the new fibre. The experimental procedure was the same as the one reported for the identification of PAC (heating-cooling-heating cycle, from 0 to 260 °C at 10 °C/min, nitrogen flow 50 ml/min, samples of about 10 mg). For comparison purposes, several calibration curves were built up.

At first, both melting peaks due to PP and PA6 on the first and second heating cycles were integrated, together with the crystallisation peaks of PP and PA6 on the cooling cycle. Comparison showed that best results were obtained integrating the melting peaks on the second heating cycles and all the results presented in this section were calculated in this way. At first analyses were performed both on untreated and pre-treated samples, however, as no differences were observed, all the subsequent analyses were performed on untreated samples. Area results in this section represent the average of three replicates. The detailed results are reported in Annex IV.

Calibration curves were built up both for PP and PA6 melting peaks, using either samples of PAC containing different PA6 content as standards, or "physical mixtures" PP - PA6 prepared in the laboratory by weighing the pure fibres. Finally, quantification based just on the comparison between enthalpies of samples and of pure PP or PA6 was also performed.

The two calibration curves prepared by using samples of PAC with different PA6 content were built up taking into account the PA6 content evaluated with elemental analysis (Fig. 21, Table 20). The blue line shows the calibration curve referring to the PP content in PAC (correlation factor 0.9971), whereas the red line shows the PA6 one (correlation factor 0.9862).

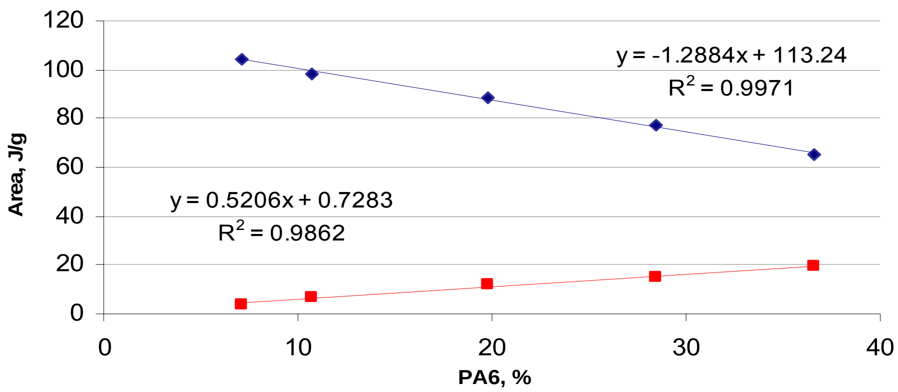


Fig. 21: Calibration curves built with PAC (samples **195 - 199**).

Table 20: Calibration curve data obtained with PAC (samples **195** - **199**).

% PA6*	Average area (J/g)	
	PP	PA6
7.11	104.07	3.56
10.72	98.60	6.67
19.83	88.65	12.15
28.45	77.32	15.28
36.57	65.29	19.44
	y=mx+n	
m =	-1.2884	0.5206
n =	113.24	0.7283
R^2 =	0.9971	0.9862

* elemental analysis

Tables 21 and 22 compare quantitative results obtained *via* elemental analysis and DSC, using the calibration curves reported in Table 20. Results showed that the PA6 content of PAC samples can be well quantified by using this approach, only when the melting peak of PP is integrated.

Table 21: Quantification of PA6 in PAC (DSC method).
(calibration curve based on PAC samples, integration of PP melting peak)

JRC code	nominal PA6 %	elemental analysis PA6 %	area J/g	DSC PA6 %	difference *vs.* elemental analysis
195	5	7.11	104.07	**7.12**	0.01
196	10	10.72	98.6	**11.37**	0.65
197	20	19.83	88.65	**19.09**	-0.74
198	30	28.45	77.32	**27.89**	-0.56
199	40	36.57	65.29	**37.23**	0.66

Table 22: Quantification of PA6 in PAC (DSC method).
(calibration curve based on PAC samples, integration of PA6 melting peak)

JRC code	nominal PA6 %	elemental analysis PA6 %	area J/g	DSC PA6 %	difference *vs.* elemental analysis
195	5	7.11	3.56	**3.31**	-3.80
196	10	10.72	6.67	**10.32**	-0.40
197	20	19.83	12.15	**22.66**	2.83
198	30	28.45	15.28	**29.71**	1.26
199	40	36.57	19.44	**39.08**	2.51

As the availability of PAC standards with various PA6 concentrations could be problematic for enforcement laboratories (only PAC 20 % is produced nowadays), two other calibration curves (Fig. 22, Table 23) were built up using samples prepared gravimetrically by mixing pure fibres of PP and PA6. The blue line shows the decrease of the PP peak area with the increase of the PA6 content in the binary mixtures (correlation factor 0.9996), whereas the red line shows the increase of the PA6 peak area with the increase of the PA6 content (correlation factor 0.9976).

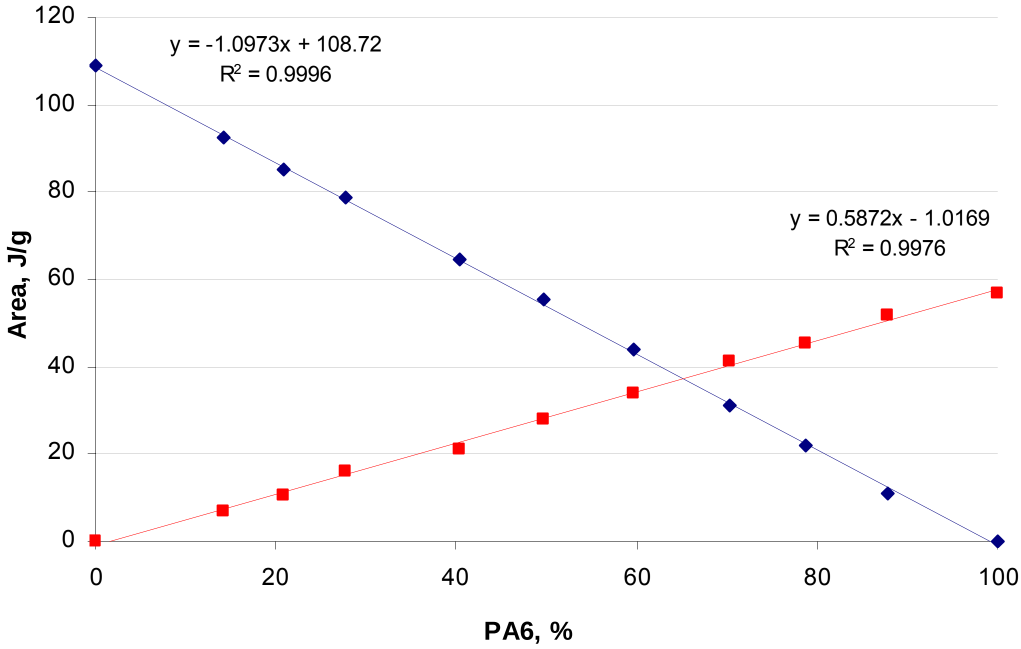


Fig. 22: Calibration curves built up with “physical mixtures” PP – PA6.

Table 23: Calibration curve data obtained with “physical mixtures” PP – PA6.

% PA6*	Area (J/g)	
	PP	PA6
0	108.80	0.00
14.22	92.72	6.74
20.88	85.13	10.69
27.79	78.57	16.07
40.39	64.77	21.27
49.67	55.41	27.88
59.55	43.76	33.71
70.23	31.12	41.31
78.82	21.77	45.15
87.74	11.15	51.90
100	0.00	56.66
y = mx+n		
m =	-1.097	0.587
n =	108.72	-1.02
R^2 =	0.9996	0.9976

* calculated from weighed mixtures PP - PA6

Table 24: Quantification of PA6 in PAC (DSC method).
(calibration curve based on "physical mixtures" PP - PA6, integration of PP melting peak)

JRC code	nominal PA6 %	elemental analysis PA6 %	area J/g	DSC PA6 %	difference *vs.* elemental analysis
195	5	7.11	104.07	**4.24**	-2.87
196	10	10.72	98.60	**9.23**	-1.49
197	20	19.83	88.65	**18.30**	-1.53
198	30	28.45	77.32	**28.62**	0.17
199	40	36.57	65.29	**39.58**	3.01

Table 25: Quantification of PA6 in PAC (DSC method).
(calibration curve based on "physical mixtures" PP - PA6, integration of PA6 melting peak)

JRC code	nominal PA6 %	elemental analysis PA6 %	area J/g	DSC PA6 %	difference *vs.* elemental analysis
195	5	7.11	3.56	**7.79**	0.68
196	10	10.72	6.67	**13.10**	2.38
197	20	19.83	12.15	**22.42**	2.59
198	30	28.45	15.28	**27.76**	-0.69
199	40	36.57	19.44	**34.83**	-1.74

As seen in Table 24, DSC results were not in good agreement with the ones obtained *via* elemental analysis, independently of the integrated melting peak, and differences up to 3 % were noticed.

Alternatively, a third approach was considered for the quantification of PA6 in PAC, taking into account the enthalpies of the pure fibres polypropylene and polyamide. In this case, the areas of PP or PA6 melting peaks in pure fibres were compared with the areas of PP or PA6 melting peaks in PAC samples. Results are shown in Tables 26 and 27.

Table 26: Quantification of PA6 in PAC based on enthalpy value of pure PP fibres (sample **192**).

JRC code	nominal PA6 %	elemental analysis PA6 %	area J/g	DSC PP %	DSC PA6 %	difference *vs.* elemental analysis
195	5	7.11	104.07	95.65	**4.35**	-2.76
196	10	10.72	98.60	90.63	**9.38**	-1.34
197	20	19.83	88.65	81.48	**18.52**	-1.31
198	30	28.45	77.32	71.06	**28.94**	0.49
199	40	36.57	65.29	60.01	**39.99**	3.42
192	0	-	**108.80**	-	**-**	-

Table 27: Quantification of PA6 in PAC based on enthalpy value of pure PA6 fibres (sample **193**).

JRC code	nominal PA6 %	elemental analysis PA6 %	area J/g	DSC PP %	DSC PA6 %	difference *vs.* elemental analysis
195	5	7.11	3.56	93.72	**6.28**	-0.83
196	10	10.72	6.67	88.22	**11.78**	1.06
197	20	19.83	12.15	78.56	**21.44**	1.61
198	30	28.45	15.28	73.03	**26.97**	-1.48
199	40	36.57	19.44	65.70	**34.30**	-2.27
193	100	-	**56.66**	-	-	-

Also in this case high differences were observed comparing to reference values. Concluding, only the first approach based on the integration of the PP melting peak and calibration curve built up with PAC samples provided good quantification results. However, the difficulty of having access to PAC samples of various PA6 content represents a serious drawback of this approach.

5.5.4 *FT-IR method*

FT-IR was proposed by the petitioner as a method for the quantification of PA6 inside PAC. As described in the section regarding the identification of the new fibre (par. 4.2), FT-IR spectra of all samples were acquired using Attenuated Total Reflectance (ATR) mode with a Perkin Elmer instrument (FT-IR spectrometer spectrum 2000). Spectra were acquired in the scan range of 4000.00-650.00 cm^{-1} at a resolution of 4.00 cm^{-1} with a total of 4 scans. Samples were analysed as received. All measurements of absorbance refer to the PA6 peak at 1650 cm^{-1}.

For the quantification of PA6 in PAC, a calibration curve was prepared using the absorbance values of samples of PAC with different PA6 content and the percentage of PA6 obtained by elemental analysis. Five replicates of each sample were analysed and results are shown in Table 28. All spectra were normalised in the entire scan range to the ordinate limit of 0.2 A (63.1 % of transmittance), so that spectra of different ordinate amplitudes could be compared. Spectra of samples analysed by FT-IR are reported in Annex III.

Table 28: Absorbance values of PA6 peak at 1650 cm^{-1} of PAC (samples **195** – **199**).

JRC code	195	196	197	198	199
% PA6*	7.11	10.72	19.83	28.45	36.57
Absorbance	0.0484	0.0778	0.1276	0.1585	0.2000
	0.0485	0.0752	0.1298	0.1746	0.2000
	0.0514	0.0780	0.1299	0.1477	0.2000
	0.0546	0.0693	0.1350	0.1807	0.2000
	0.0445	0.0649	0.1260	0.1774	0.2000
average	0.0495	0.0731	0.1297	0.1678	0.2000
SD	0.004	0.006	0.003	0.014	-
RSD %	7.66	7.88	2.62	8.39	-

* quantification based on elemental analysis

The above data were used to build up the linear calibration curve shown in Fig. 23. The *y*-residuals were calculated (Table 29) and their plot is presented in Fig. 24.

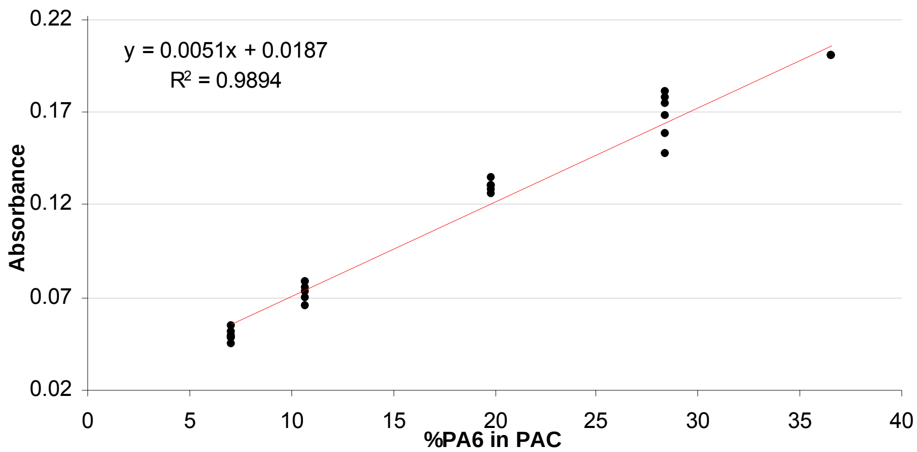


Fig 23: Linear calibration curve built-up with PAC (samples **195** – **199**).

Table 29: *Y*-residual values calculated based on the linear calibration curve.

	Linear calibration: y = ax + b				
JRC code	195	196	197	198	199
% PA6*	7.11	10.72	19.83	28.45	36.57
estimated % PA6	6.01	10.60	21.65	29.07	35.35
y-residual	-1.10	-0.12	1.82	0.62	-1.22

* quantification based on elemental analysis

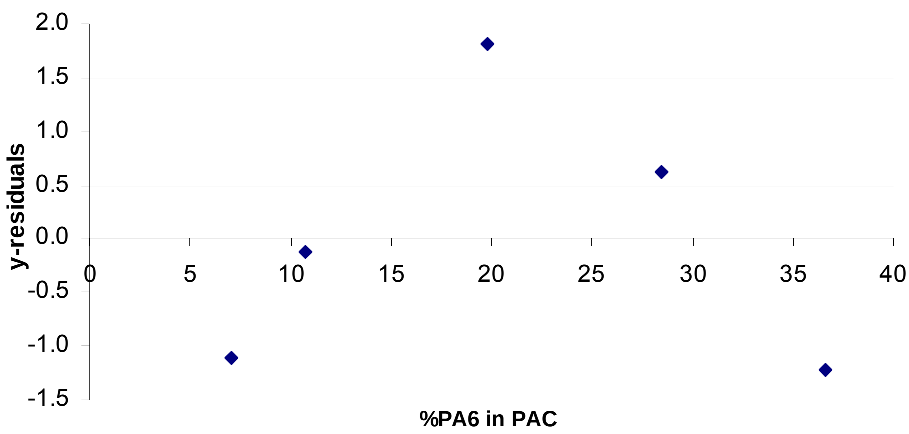


Fig 24: *Y*-residuals plot based on the linear calibration curve.

The *y*-residuals showed a trend in the signs and magnitudes; at first they were negative at low *x*-values, then they reached a positive maximum and, finally, they became again negative. This fact suggested that a quadratic calibration curve should be plotted (Fig. 25). According to this curve, the *y*-residuals were calculated (Table 30) and their plot is presented in Fig. 26.

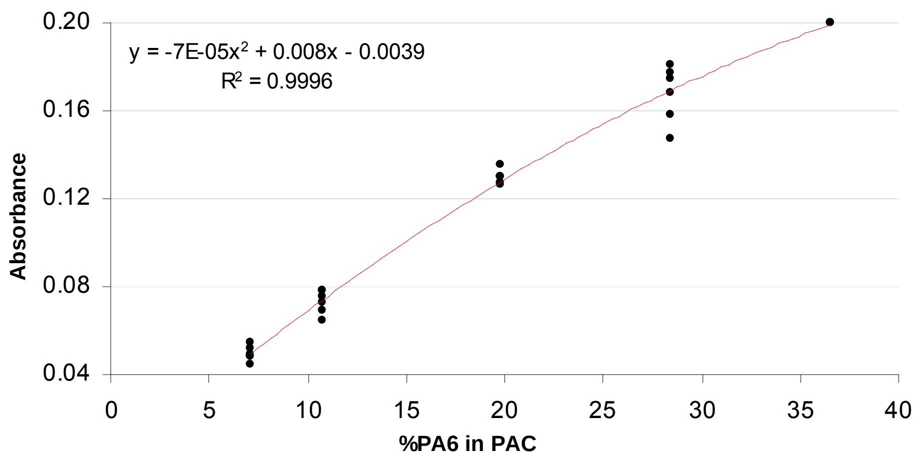


Fig 25: Quadratic calibration curve built-up with PAC (samples **195** – **199**).

Table 30: *Y*-residual values calculated based on the quadratic calibration curve.

	Quadratic calibration: $y = ax^2 + bx + c$				
JRC code	**195**	**196**	**197**	**198**	**199**
% PA6*	**7.11**	**10.72**	**19.83**	**28.45**	**36.57**
estimated % PA6	7.13	10.61	20.14	28.07	36.74
y-residual	**0.02**	**-0.11**	**0.31**	**-0.38**	**0.17**

* quantification based on elemental analysis

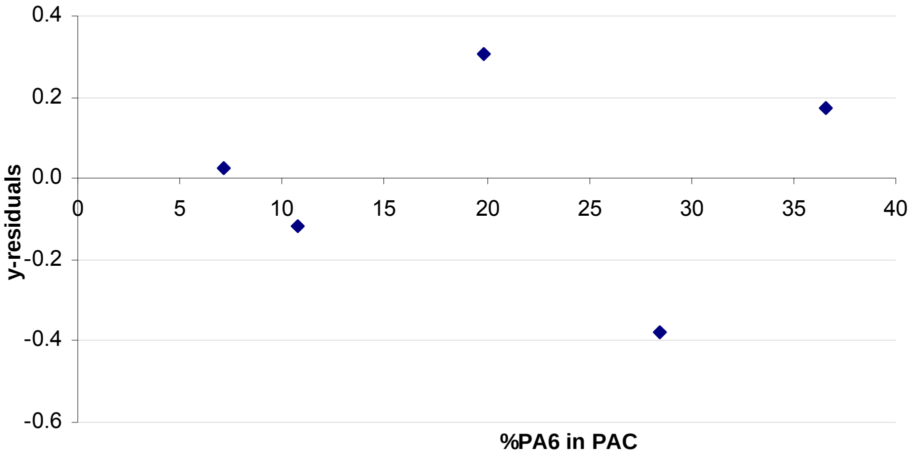


Fig 26: *Y*-residuals plot based on the quadratic calibration curve.

The distribution of *y*-residuals in the case of the quadratic calibration curve could be considered satisfactory. In order to check the accuracy of FT-IR as a technique to quantify PA6 in PAC, five replicates of sample **233** (PAC 20 %) were analysed using both the linear (Fig. 23) and the quadratic (Fig. 25) calibration curves. Results were compared to the ones obtained by elemental analysis (Tables 31 and 32).

Table 31: Absorbance values of PA6 peak at 1650 cm^{-1} of PAC (sample **233**).

JRC code	233
Absorbance	0.1304
	0.1266
	0.1354
	0.1270
	0.1255
average	**0.1290**
SD	0.004
RSD %	3.12

Table 32: Quantification of PAC (sample **233**) using linear and quadratic calibration curves.

JRC code	linear	quadratic
% PA6*	**19.85**	**19.85**
estimated % PA6	21.51	20.01
difference	**1.66**	**0.16**

* quantification based on elemental analysis

The FT-IR technique presented results very similar to the ones obtained by elemental analysis, especially when the quadratic calibration curve was used. Nevertheless, the disadvantage of the need to possess standards of PAC of various concentrations to build-up the calibration curve cannot be neglected.

5.5.5 *Chemical methods*

Chemical dissolution methods were applied by the JRC in order to find alternative methods for the quantification of PA6 in PAC, which do not require the availability of PAC standards. With the intention to dissolve the polyamide component of the fibre, the tested chemical methods were based on formic acid solutions of different concentration, applying various conditions of time and temperature. Results were compared with the ones obtained by elemental analysis (Table 33).

From the theoretical point of view, any chemical method able to dissolve polyamide but not polypropylene, will most probably not be capable to dissolve the part of PA6 chemically linked to polypropylene through the compatibiliser. For this reason, results were expected to be lower than the reference values obtained *via* elemental analysis.

Table 33: Quantification of PA6 in PAC (comparison of chemical methods).

JRC Code	% PA6 *		Method					
			A	B	C	D	E	F
199	36.57 %	n	25	2	5	3	3	14
		PA6 %	35.18	34.68	34.68	33.10	33.15	33.02
		conf. limit (95%)	0.10	0.68	0.48	0.39	0.42	0.15
198	28.45 %	n	20	5	3	-	-	10
		PA6 %	27.61	27.20	26.89	-	-	18.58
		conf. limit (95%)	0.05	0.46	0.05	-	-	0.77
197	19.83 %	n	20	5	5	-	-	9
		PA6 %	18.78	18.27	17.69	-	-	1.24
		conf. limit (95%)	0.11	0.33	0.40	-	-	0.24
196	10.72 %	n	19	3	6	-	-	9
		PA6 %	8.94	8.89	5.26	-	-	0.40
		conf. limit (95%)	0.02	0.70	1.46	-	-	0.10
195	7.11 %	n	20	8	2	-	-	10
		PA6 %	4.20	2.19	2.28	-	-	0.26
		conf. limit (95%)	0.02	0.41	16.15	-	-	0.09

* % PA6 based on elemental analysis

	Conditions					
	A	B	C	D	E	F
HCOOH	90 %	98-100 %	98-100 %	80 %	80 %	80 %
Time	1 h	3 h	15 min	7 h	1 h	15 min
T	90 °C	RT*	RT	RT	RT	RT

Note 1: Method A is method 16 of Directive 96/73/EC.

Note 2: Method F is method 4 of Directive 96/73/EC.

*** RT:** room temperature

Among all the tested methods, method 16 of Directive 96/73/EC (condition A) gave the most similar results to the reference values. This evidence suggested that a combination of high concentration of formic acid and high temperature is needed to reach and dissolve the PA6 fibrils shielded by polypropylene in PAC. Method 16 showed differences always negative, as expected, and not higher than 2 %. The only exception was in the case of sample **195**, but the reference value for this sample was most probably affected by errors; in fact, it was the only one showing high differences between the results for the two replicates (see Table 18).

Table 34: Quantification of PA6 in PAC (method 16).

JRC code	nominal PA6 %	elemental analysis PA6 %	hot formic acid method			difference *vs.* elemental analysis
			PA6 %	conf. limit (95%)	replicates	
195	5	7.11	**4.20**	0.02	20	-2.91
196	10	10.72	**8.94**	0.02	19	-1.78
197	20	19.83	**18.78**	0.11	20	-1.05
198	30	28.45	**27.61**	0.05	20	-0.84
199	40	36.57	**35.18**	0.10	25	-1.39
233	20	19.85	**18.83**	0.17	5	-1.02

Additionally, PAC samples were analysed with method 13 of Directive 96/73/EC, in an attempt to dissolve the PP component of PAC, instead of the PA6 one (Table 35). Even though filters were warmed in the oven before use, strong difficulties were experienced principally to avoid the reprecipitation of the dissolved PP component while filtering. In some cases, filtration was not possible at all, due to the occlusion of the filter, most probably not only due to the reprecipitation of PP, but also to the PA component that had the appearance of a thin plastic film. Problems were also noticed because of the lack of repeatability.

Table 35: Quantification of PA6 in PAC (method 13).

JRC code	nominal PA6 %	elemental analysis PA6 %	method 13			difference *vs.* elemental analysis
			PA6 %	conf. limit (95%)	replicates	
195	5	7.11	**5.11**	0.25	5	-2.00
196	10	10.72	**11.29**	0.35	5	0.57
197	20	19.83	**20.04**	0.59	5	0.21
198	30	28.45	**29.99**	0.22	5	1.54
199	40	36.57	**40.22**	0.23	8	3.65

In Table 35 only the best results are reported. They showed to be always higher than the reference values, except for sample **195**, confirming the idea that it was not possible to avoid completely the reprecipitation of PP on the filter. In the case of sample **199**, the difference was as high as 3.6 %. As a result, method 13 was excluded as a possible chemical quantitative method, due to the risk of overestimating the PA6 content in PAC.

Concluding, among the tested chemical methods, method 16 resulted to be the one with the highest accuracy, when compared with the results obtained *via* elemental analysis, and it was proposed by the JRC for the quantification of PA6 in PAC.

5.6 Quantification of binary mixtures PA6/PAC and PP/PAC

5.6.1 *Manual separation*

Binary mixtures made with twisted yarns were quantified *via* manual separation. Manual separation of binary mixtures made with interlaced yarns was not feasible, because the two fibres had the same colour (white).

The values of *agreed allowance* used for the calculation of results were 1.00 % for PAC, 2.00 % for PP and 5.75 % for PA6 (as the PA6 fibres of the binary mixture PA6/PAC were considered filaments). Results are listed in Table 36 and compared with the theoretical contents of PAC calculated based on linear density measurements, performed by Aquafil, on the pure fibres.

Table 36: Quantification of binary mixtures (manual separation).

JRC code	composition	manufacturing type	theoretical (Aquafil) PAC %	manual separation			
				n	PAC %	conf. limit (95 %)	difference *vs.* theoretical
201	PA6/PAC (10 %)	twisted	47.1	10	**46.03**	0.29	-1.07
203	PA6/PAC (20 %)	twisted	47.4	10	**46.37**	0.44	-1.03
205	PA6/PAC (30 %)	twisted	47.7	10	**46.81**	0.50	-0.89
206	PA6/PAC (40 %)	twisted	47.7	9	**46.47**	0.56	-1.23
208	PP/PAC (10 %)	twisted	50.1	10	**49.50**	0.40	-0.60
210	PP/PAC (20 %)	twisted	50.4	10	**49.73**	0.32	-0.67
212	PP/PAC (30 %)	twisted	50.7	10	**49.87**	0.47	-0.83
213	PP/PAC (40 %)	twisted	50.8	10	**50.45**	0.49	-0.35

Quantification results based on manual separation were in very good agreement with the theoretical ones. Whenever possible, manual separation is recommended as it is considered more precise and accurate than other analyses, such as the chemical ones. For this reason, PAC contents estimated through manual separation were considered as reference values against which results obtained with alternative methods were compared. For comparison purposes, the interlaced binary mixtures (samples **200**, **202**, **204**, **207**, **209** and **211**) were considered to be of the same composition as the respective twisted ones.

Carpet samples sent by Aquafil containing PA6 (beige) and PAC (white) were both loop type (samples **234** – **239**) and cut type (samples **240** – **245**). Similarly, carpet samples containing PP (black) and PAC (white) were loop type (samples **246** – **251**) and cut type (samples **252** – **257**). Half of the samples were manufactured containing twisted yarns and the other half interlaced ones. An example of carpet samples can be seen in Fig. 27.

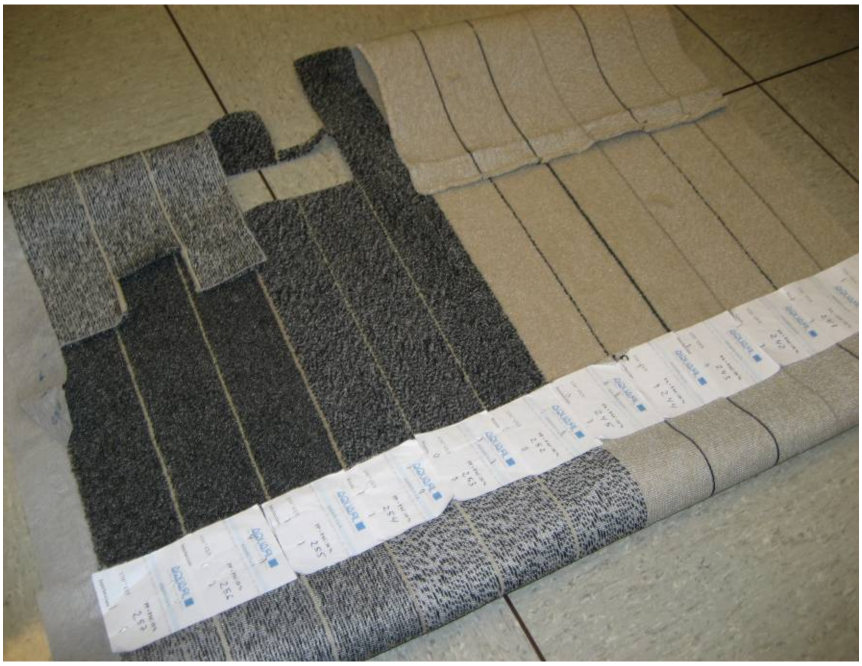


Fig. 27: Cut carpet samples PP/PAC (samples **252** – **257**) and PA6/PAC (samples **240** – **245**).

Carpet samples were manually separated in order to obtain reference values against which compare other quantitative results (Tabs. 37-38). All loop carpet samples containing both twisted and interlaced yarns were analysed *via* manual separation. Manual separation of cut samples was not possible in the case of interlaced yarns. In the case of twisted yarns, this technique has the disadvantage to be very time-consuming and applicable only in the case of mixtures containing fibres of different colour.

Table 37: Quantification of carpet samples PA6/PAC (manual separation).

	JRC code	nominal PA6 in PAC %				manual separation		
						n	PAC %	conf. limit (95 %)
Carpet 1	234	30	PA beige + PAC white	LOOP	twisted	10	47.74	0.36
Carpet 1	235	20	PA beige + PAC white	LOOP	twisted	10	46.53	0.30
Carpet 1	236	10	PA beige + PAC white	LOOP	twisted	10	46.35	0.35
Carpet 1	237	30	PA beige + PAC white	LOOP	Interl.	10	46.66	0.39
Carpet 1	238	20	PA beige + PAC white	LOOP	Interl.	10	46.54	0.45
Carpet 1	239	10	PA beige + PAC white	LOOP	Interl.	10	46.50	0.53
Carpet 2	240	30	PA beige + PAC white	CUT	twisted	-	-	-
Carpet 2	241	20	PA beige + PAC white	CUT	twisted	-	-	-
Carpet 2	242	10	PA beige + PAC white	CUT	twisted	-	-	-
Carpet 2	243	30	PA beige + PAC white	CUT	Interl.	-	-	-
Carpet 2	244	20	PA beige + PAC white	CUT	Interl.	-	-	-
Carpet 2	245	10	PA beige + PAC white	CUT	Interl.	-	-	-

Table 38: Quantification of carpet samples PP/PAC (manual separation).

	JRC code	nominal PA6 in PAC %				manual separation n	PAC %	conf. limit (95 %)
Carpet 1	246	30	PP black + PAC white	LOOP	twisted	10	56.64	0.37
	247	20				10	56.94	0.48
	248	10				10	56.53	0.18
	249	30			Interl.	10	56.36	0.34
	250	20				10	56.24	0.38
	251	10				10	55.72	0.60
Carpet 2	252	30		CUT	twisted	8	56.41	0.14
	253	20				8	56.42	0.31
	254	10				8	56.15	0.10
	255	30			Interl.	-	-	-
	256	20				-	-	-
	257	10				-	-	-

5.6.2 *DSC method*

The DSC technique was proposed by the petitioner for the quantification of binary mixtures of PAC with PP or PA6. Using the same experimental procedure and the same approach as in the quantification of PA6 in PAC, two calibration curves were built up: the first one made with PAC samples (see Fig. 21) and the second one made with "physical mixtures" of pure PP and PA6 fibres (see Fig. 22). The areas (J/g) of PP and PA6 melting peaks were averaged on the basis of three replicates. Detailed results are reported in Annex IV.

If the percentage of PA6 in PAC is known, binary mixtures PP/PAC or PA6/PAC can be quantified using the value of total percentage of PA6 in the sample, measured with DSC. The percentage of PAC is calculated back in the following way.

For binary mixtures PA6/PAC:

$$\%PAC = 100\frac{\%PP_t}{\%PP_i} = 100\frac{100-\%PA6_t}{100-\%PA6_i} \qquad 5.6.2.1$$

and for binary mixtures PP/PAC:

$$\%PAC = 100\frac{\%PA6_t}{\%PA6_i} \qquad 5.6.2.2$$

where

% PAC	is the percentage of PAC in the binary mixture,
% PP_i	is the percentage of PP in PAC,
% PP_t	is the total percentage of PP in the binary mixture,
% $PA6_i$	is the percentage of PA6 in PAC,
% $PA6_t$	is the total percentage of PA6 in the binary mixture.

The quantification results obtained using the calibration curve built up with "physical mixtures" of PP and PA6 (see Fig. 22) are shown in Tables 39 and 40. The *% $PA6_i$* values, obtained by elemental analysis, were used as input in the calculations. It has to be reminded that manual separation could be performed only on twisted samples (**201**, **203**, **205**, **206**, **208**, **210**, **212** and **213**) and that, for comparison purposes, the interlaced samples were supposed to be of equal composition to the respective twisted ones.

Table 39: Quantification of binary mixtures PA6/PAC.
(calibration curve based on "physical mixtures" PP - PA6)

JRC code	elem. analysis PA6 %	man sep PAC %	PP J/g	PA6 J/g	based on PP area PA6 tot %	based on PP area PAC %	diff. *vs.* man sep	based on PA6 area PA6 tot %	based on PA6 area PAC %	diff. *vs.* man sep
200	10.72	-	39.22	31.36	63.34	**41.07**	-4.96	55.14	**50.25**	4.22
201	10.72	46.03	38.65	32.71	63.86	**40.48**	-5.55	57.43	**47.68**	1.65
202	19.83	-	37.45	33.37	64.95	**43.72**	-2.65	58.55	**51.70**	5.33
203	19.83	46.37	37.10	34.67	65.27	**43.32**	-3.05	60.77	**48.94**	2.57
204	28.45	-	31.32	35.25	70.54	**41.18**	-5.63	61.76	**53.45**	6.64
205	28.45	46.81	31.35	35.84	70.51	**41.22**	-5.59	62.76	**52.05**	5.24
206	36.57	46.47	28.72	37.69	72.91	**42.71**	-3.76	65.91	**53.74**	7.27

Table 40: Quantification of binary mixtures PP/PAC.
(calibration curve based on "physical mixtures" PP - PA6)

JRC code	elem. analysis PA6 %	man sep PAC %	PP J/g	PA6 J/g	based on PP area PA6 tot %	based on PP area PAC %	diff. *vs.* man sep	based on PA6 area PA6 tot %	based on PA6 area PAC %	diff. *vs.* man sep
207	10.72	-	99.91	3.16	8.04	**74.96**	25.46	7.12	**66.41**	16.91
208	10.72	49.50	97.65	3.17	10.09	**94.11**	44.61	7.14	**66.57**	17.07
209	19.83	-	93.45	5.44	13.92	**70.19**	20.46	10.99	**55.41**	5.68
210	19.83	49.73	94.41	5.28	13.04	**65.76**	16.03	10.72	**54.05**	4.32
211	28.45	-	94.87	7.49	12.63	**44.39**	-5.48	14.49	**50.93**	1.06
212	28.45	49.87	94.72	7.41	12.76	**44.85**	-5.02	14.35	**50.44**	0.57
213	36.57	50.45	89.48	9.95	17.54	**47.97**	-2.48	18.68	**51.08**	0.63

Apart from few exceptions, quantification results were not accurate. Both for binary mixtures with PA6 and PP, high differences were calculated comparing with the reference values, independently of the melting peak integrated.

Using the same approach for the calculation of results, the quantification results of binary mixtures PA6/PAC and PP/PAC, using the calibration curve built up with PAC samples (see Fig. 21), are shown in Tables 41 and 42.

Table 41: Quantification of binary mixtures of PA6/PAC.
(calibration curve based on PAC samples)

JRC code	elem. analysis PA6 %	man sep PAC %	PP J/g	PA6 J/g	based on PP area		diff.	based on PA6 area		diff.
					PA6 total %	PAC %	*vs.* man sep	PA6 total %	PAC %	*vs.* man sep
200	10.72	-	39.22	31.36	57.45	**47.66**	1.63	58.84	**46.10**	0.07
201	10.72	46.03	38.65	32.71	57.90	**47.16**	1.13	61.42	**43.21**	-2.82
202	19.83	-	37.45	33.37	58.82	**51.36**	4.99	62.69	**46.54**	0.17
203	19.83	46.37	37.10	34.67	59.10	**51.02**	4.65	65.19	**43.42**	-2.95
204	28.45	-	31.32	35.25	63.58	**50.90**	4.09	66.31	**47.09**	0.28
205	28.45	46.81	31.35	35.84	63.56	**50.93**	4.12	67.43	**45.51**	-1.30
206	36.57	46.47	28.72	37.69	65.60	**54.23**	7.76	70.99	**45.73**	-0.74

Table 42: Quantification of binary mixtures of PP/PAC.
(calibration curve based on PAC samples)

JRC code	elem. analysis PA6 %	man sep PAC %	PP J/g	PA6 J/g	based on PP area		diff.	based on PA6 area		diff.
					PA6 total 5	PAC %	*vs.* man sep	PA6 total %	PAC %	*vs.* man sep
207	10.72	-	99.91	3.16	10.35	**96.56**	47.06	4.68	**43.64**	-5.86
208	10.72	49.50	97.65	3.17	12.10	**112.86**	63.36	4.70	**43.81**	-5.69
209	19.83	-	93.45	5.44	15.36	**77.47**	27.74	9.04	**45.60**	-4.13
210	19.83	49.73	94.41	5.28	14.61	**73.70**	23.97	8.74	**44.06**	-5.67
211	28.45	-	94.87	7.49	14.26	**50.13**	0.26	12.99	**45.67**	-4.20
212	28.45	49.87	94.72	7.41	14.38	**50.53**	0.66	12.83	**45.11**	-4.76
213	36.57	50.45	89.48	9.95	18.45	**50.44**	-0.01	17.72	**48.45**	-2.00

In the case of binary mixtures PA6/PAC, best results were obtained with the integration of the PA6 peak. Generally, good quantification could be achieved with the exception of two samples (**201** and **203**, PAC 10 % and 20 % respectively).

In the case of binary mixtures PP/PAC, differences obtained between DSC and manual separation results were very high, apart from samples with high PA6 content integrating the PP melting peak.

Alternatively, a third approach was performed for the quantification of binary mixtures PP/PAC and PA6/PAC, taking into account the enthalpies of the pure fibres PP and PA6, as in the case of the quantification of PA6 in PAC. For the calculation of results, formulas 5.6.2.1 and 5.6.2.2 were used, where:

$$\%PA6_t = 100\frac{PA6_{(J/g)}}{PA6_{100\%}} \qquad 5.6.2.3$$

in the case of integration based on the PA6 peak and

$$\%PA6_t = 100 - \%PP_t = 100 - \left[100 \frac{PP_{(J/g)}}{PP_{100\%}} \right] \qquad 5.6.2.4$$

in the case of integration based on the PP peak.

Table 43: Quantification of binary mixtures PA6/ PAC,
based on enthalpy values of pure PP (sample **192**) and PA6 (sample **193**).

JRC code	elem. analysis PA6 %	man sep PAC %	PP J/g	PA6 J/g	based on PP area PP total %	PA6 total %	PAC %	diff. *vs.* man sep	based on PA6 area PA6 tota %l	PAC %	diff. *vs.* man sep
200	10.72	-	39.22	31.36	36.05	63.95	**40.38**	-5.65	55.35	**50.01**	3.98
201	10.72	46.03	38.65	32.71	35.52	64.48	**39.79**	-6.24	57.72	**47.35**	1.32
202	19.83	-	37.45	33.37	34.42	65.58	**42.94**	-3.43	58.89	**51.28**	4.91
203	19.83	46.37	37.10	34.67	34.10	65.90	**42.53**	-3.84	61.18	**48.42**	2.05
204	28.45	-	31.32	35.25	28.79	71.21	**40.23**	-6.58	62.21	**52.81**	6.00
205	28.45	46.81	31.35	35.84	28.82	71.18	**40.28**	-6.53	63.25	**51.36**	4.55
206	36.57	46.47	28.72	37.69	26.40	73.60	**41.62**	-4.85	66.52	**52.78**	6.31

Table 44: Quantification of binary mixtures PP/ PAC,
based on enthalpy values of pure PP (sample **192**) and PA6 (sample **193**).

JRC code	elem. analysis PA6 %	man sep PAC %	PP J/g	PA6 J/g	based on PP area PP total %	PA6 total %	PAC %	diff. *vs.* man sep	based on PA6 area PA6 total %	PAC %	diff. *vs.* man sep
207	10.72	-	99.91	3.16	91.82	8.18	**76.26**	26.76	5.58	**52.09**	2.59
208	10.72	49.50	97.65	3.17	89.75	10.25	**95.57**	46.07	5.60	**52.25**	2.75
209	19.83	-	93.45	5.44	85.89	14.11	**71.15**	21.42	9.59	**48.38**	-1.35
210	19.83	49.73	94.41	5.28	86.78	13.22	**66.68**	16.95	9.31	**46.96**	-2.77
211	28.45	-	94.87	7.49	87.19	12.81	**45.01**	-4.86	13.22	**46.48**	-3.39
212	28.45	49.87	94.72	7.41	87.06	12.94	**45.49**	-4.38	13.08	**45.97**	-3.90
213	36.57	50.45	89.48	9.95	82.24	17.76	**48.57**	-1.88	17.57	**48.03**	-2.42

As presented in Table 23 (see par. 5.5.3), the enthalpies of pure PA6 ($PA6_{100\%}$) and pure PP ($PP_{100\%}$) were 56.66 J/g and 108.8 J/g, respectively. Results regarding the quantification of binary mixtures PA6/PAC and PP/PAC based on the comparison of the enthalpies of the binary mixtures and those of pure PA6 and PP are shown in Tables 43 and 44. Neither with the third approach good quantitative results could be obtained.

Based on all these experimental data, it can be concluded that the DSC method is not accurate enough to quantify binary mixtures PA6/PAC and PP/PAC. In fact, results were far different from the reference values obtained *via* manual separation.

5.6.3 *Chemical analysis*

5.6.3.1 *Method 11 of Directive 96/73/EC*

Binary mixtures of PA6/PAC were analysed with method 11 of Directive 96/73/EC, as PA6 fibrils inside the new fibre are not soluble with 75 % sulphuric acid at room temperature, whereas PA6 fibres in mixture with PAC are. The values of *agreed allowance* used for the calculation of results were 1.00 % for PAC and 5.75 % for PA6 (filament). According to the analysis performed on PAC samples (Tabs. 12 and 17), the *d* factor used for the calculation of results regarding binary mixtures was 1.01.

Table 45: Quantification of PAC in binary mixtures PA6/PAC (method 11).

JRC code	nominal PA6 in PAC %	manuf. type	manual separation PAC %	method 11			
				n	PAC %	conf. limit (95%)	difference *vs.* manual separation
200	10	interlaced	-	9	**46.87**	0.24	0.84
201	10	twisted	46.03	10	**46.16**	0.30	0.13
202	20	interlaced	-	10	**47.78**	0.33	1.41
203	20	twisted	46.37	10	**47.15**	0.23	0.78
204	30	interlaced	-	10	**47.29**	0.79	0.48
205	30	twisted	46.81	10	**47.28**	0.26	0.47
206	40	twisted	46.47	9	**46.91**	1.27	0.44

Table 45 contains the quantitative results of binary mixtures PA6/PAC, as well as their comparison with the reference values. It has to be reminded that manual separation could be performed only on twisted samples (**201**, **203**, **205** and **206**) and that the respective interlaced samples were supposed to be of equal composition for comparison purposes. Results were similar to the ones obtained *via* manual separation, showing a difference of less than 1 % in most cases.

Carpet samples PA6/PAC were also quantified and results (Table 46) were in very good agreement with the ones obtained *via* manual separation, showing differences of less than 1 %. Therefore, it was concluded that method 11 is an accurate method for the quantification of PAC in binary mixtures PA6/PAC, both yarns and carpets.

Table 46: Quantification of carpets samples PA6/PAC (method 11).

	JRC code	nominal PA6 in PAC %				manual separation PAC %	method 11 n	method 11 PAC %	method 11 conf. limit (95 %)	method 11 difference *vs.* manual separation
Carpet 1	**234**	30	PA / PAC	LOOP	twisted	47.74	5	**47.74**	0.51	0.00
	235	20				46.53	5	**46.80**	0.65	0.27
	236	10				46.35	5	**47.10**	1.88	0.75
	237	30			Interl.	46.66	4	**47.37**	0.39	0.71
	238	20				46.54	5	**46.68**	0.94	0.14
	239	10				46.50	5	**46.77**	0.60	0.27

5.6.3.2 *Method 16 of Directive 96/73/EC*

Binary mixtures of PP/PAC were analysed with method 16 of Directive 96/73/EC, which is able to solubilise PA6 fibrils inside PAC. If the percentage of PA6 in PAC is known, binary mixtures PP/PAC can be quantified by calculating the total percentage of PA6 in the binary mixture obtained with method 16. Then, the percentage of PAC in the binary mixture is calculated back using the formula 5.6.2.2. In the case of this experimental study, as Aquafil had provided the JRC with the PAC yarns used in the production of the binary mixtures, the percentage of PA6 in PAC, needed as input data in the above formula, was obtained applying method 16 to the PAC samples **195** – **199**. The values of *agreed allowance* used for the calculation of results with this method were 2.00 % for PP and 6.25 % for PA6 inside PAC (considered as discontinuous fibre).

Table 47: Quantification of PAC in binary mixtures PP/PAC (method 16).

JRC code	nominal PA6 in PAC %	manuf. type	manual separation PAC %	method 16					
				n	PA6 in binary mixtures %	conf. limit (95%)	PA6 in PAC %	PAC %	difference *vs.* manual separation
207	10	interlaced	-	9	4.56	0.17	8.94	50.97	1.47
208	10	twisted	49.50	10	4.41	0.05		49.36	-0.14
209	20	interlaced	-	10	9.51	0.10	18.78	50.66	0.93
210	20	twisted	49.73	10	9.44	0.14		50.28	0.55
211	30	interlaced	-	9	14.03	0.05	27.61	50.82	0.95
212	30	twisted	49.87	9	14.09	0.05		51.04	1.17
213	40	twisted	50.45	10	18.15	0.32	35.18	51.60	1.15

Table 47 contains the results of the quantification of PAC in binary mixtures PP/PAC, as well as their comparison with the reference values. Attention must be paid to the fact that manual separation could be performed only on twisted samples (**208**, **210**, **212** and **213**) and that the respective interlaced samples were supposed to be of equal composition for comparison purposes. Results appeared to be in good agreement with the quantification performed *via* manual separation. Differences were less than 1.5 % in all cases.

For the quantification of carpets PP/PAC, samples were firstly manually separated; then, the PAC part was analysed with method 16 in order to obtain the percentage of PA6 inside PAC (*% PA6*$_i$). The total % PA6 in the carpet samples (*% PA6*$_t$) was also measured by method 16 and these two percentages of PA6 were used for the quantification of PAC in the carpet samples using the formula 5.6.2.2.

Table 48: Quantification of carpets samples PP/PAC (method 16).

	JRC code	nominal PA6 in PAC %				manual separation PAC %	method 16							
							n	PA6 in PAC %	conf. limit (95 %)	n	PA6 in carpet %	conf. limit (95 %)	PAC %	difference *vs.* manual separation
Carpet 1	**246**	30	PP / PAC	LOOP	twisted	56.64	5	27.79	0.11	5	16.07	0.15	57.83	1.19
	247	20				56.94	5	18.89	0.12	5	10.94	0.07	57.90	0.96
	248	10				56.53	5	8.84	0.07	5	5.07	0.13	57.39	0.86
	249	30			Interl.	56.36	5	27.58	0.05	5	15.97	0.29	57.91	1.55
	250	20				56.24	5	18.52	0.09	5	10.54	0.24	56.91	0.67
	251	10				55.72	5	8.86	0.07	5	5.00	0.19	56.40	0.68
Carpet 2	**252**	30		CUT	twisted	56.41	3	27.76	0.05	2	16.09	0.55	57.95	1.54
	253	20				56.42	3	18.68	0.03	2	10.79	0.19	57.76	1.34
	254	10				56.15	3	8.85	1.08	2	4.99	1.36	56.35	0.20
	255	30			Interl.	-	-	-	-	6	15.77	0.05	-	-
	256	20				-	-	-	-	5	10.67	0.08	-	-
	257	10				-	-	-	-	6	5.15	0.05	-	-

In general, results obtained with method 16 were in line with the ones obtained *via* manual separation, showing differences of up to 1.55 %.
Concluding, method 16 was proved to be a method sufficiently accurate for the quantification of binary mixtures PP/PAC, including real carpet samples, provided that the PA6 content of PAC is known or a quantity of PAC can be separated from the mixture and analysed to obtain this value.

5.6.4 Densitometric method combined with method 16 of Dir. 96/73/EC

In an attempt to find a way to separate PAC from mixtures PP/PAC, when manual separation is not feasible, in order to be able to quantify its PA6 content applying method 16 on it, a variation of a densitometric method proposed by industry (see Annex I) was investigated. The physical separation of PAC from the binary mixture was based on the difference of densities between PAC (0.93-0.98 g/cm^3) and PP (0.89-0.905 g/cm^3). Using an ethanol/water solution of density 0.92 g/cm^3, the less dense fibre PP would float on the surface of the liquid, whereas the densest fibre PAC would go to the bottom.
The yarns of the binary mixture were cut into pieces not longer than 5 mm; entangling knots were removed and single filaments were physically separated. 50 mg of cut yarns were placed in a bottle of 500 ml and then 400 ml of the ethanol/water solution (0.92 g/cm^3), prepared at least two days before, were added. Mixing was performed until all fibres were wet and separated one from the other. The floating fibres were removed after 24 h and the solution was filtered to collect the fibres of the bottom. The filter with the residue was dried overnight (14-16 h) in a vacuum oven, left in dessicator for 2 h and then weighed.
Due to the fact that the densitometric method requires big quantities of ethanol, the ratio (sample size)/(volume of solution needed) had to be optimised; experimental tests proved that the optimal ratio was 100 mg of binary mixture PP/PAC per 200 ml of solution ethanol/water (90:130 v/v). Since the densitometric method was very time-consuming and several separations were needed in order to collect one gram of PAC, experiments were performed applying method 16 of Directive 96/73/EC to evaluate the minimum quantity of PAC sample needed for an accurate determination of PA6 in PAC. Sample sizes were decreased from one gram (reference value) to one hundred

milligrams; in parallel also the reagent volume was adjusted. First results showed that accuracy was worsened lowering sample size. This effect could be avoided using small and light glassware. As shown in Table 49, using small filters and weighing bottles, 100 mg of pure PAC in 50 ml of formic acid solution are sufficient in order to obtain results enough accurate.

Table 49: Quantification of PA6 in PAC, influence of sample size (method 16).

JRC code	method 16 PA6 %	sample mass g	volume reagent ml	weighing bottle mass g	weighing filter mass g	n	PA6 %	conf. limit (95 %)	diff.
199	35.18	0.500	100	68	32	3	**35.36**	0.48	-0.18
199	35.18	0.250	50	68	32	3	**35.52**	0.36	-0.34
199	35.18	0.200	40	68	32	3	**35.59**	0.20	-0.41
199	35.18	0.150	30	68	32	3	**36.51**	1.18	-1.33
199	35.18	0.100	20	68	32	3	**35.98**	0.11	-0.80
199	35.18	0.100	50	68	32	9	**36.39**	0.07	-1.21
199	35.18	0.250	50	20	19	9	**35.18**	0.05	0.00
199	35.18	0.100	50	20	19	10	**35.37**	0.05	-0.19

In the case of a binary mixture PP/PAC about 50/50, the densitometric method would need to be applied five times, using the optimised ratio mg of sample per ml of solution, in order to collect about 200 mg of PAC, so that two replicates (100 mg each) could be analysed with method 16.

Unfortunately, from the experimental point of view, several problems were observed in particular due to lack of repeatability. Firstly, the fibres were prone to stay together, despite careful sample preparation; secondly, the same ethanol/water solution worked differently on different specimens of the same sample; thirdly, bubbles were evident in the solution and disturbed the process. Last but not least, the removal of the floating fibres had to be repeated twice with an interval of six hours, as the removal of the fibres caused perturbation of the solution and, thus, problems in separation.

The densitometric method was applied to the black/white carpet sample **255** (PP/PAC 30 %) to separate a quantity of PAC from the binary mixture. Subsequently, method 16 was performed on the separated PAC fibres (sample **255***) and results are shown in Table 50.

Table 50: Quantification of PA6 in PAC (method 16).
PAC separated from sample **255** (densitometric method).

JRC code	reference value PA6 (HFA) %	sample mass g	volume reagent ml	n	PA6 %	conf. limit (95 %)	difference
255*	27.61	0.150	50	5	**27.52**	0.16	0.09

The quantification of PA6 in PAC in sample **255*** was very good; however, several major disadvantages were observed. First of all the entire procedure was very time-consuming; in fact, apart from the 24 plus 6 h contact time, five separations were needed in order to obtain the minimum quantity needed for the subsequent execution of method 16. Moreover, a perfect separation between PAC and PP could not be achieved, as evident due to the different colours of the fibres. Last but not least, there was an evident lack of repeatability in the experimental procedure. Therefore, the densitometric method was judged not adequate to separate PAC sample from binary mixtures PP/PAC as a first step towards the quantification of binary mixtures PP/PAC with method 16.

6. Collaborative trial

As agreed on 10th December 2010, during the 10th meeting of the European network of national experts on Textile Labelling (ENNETL), the JRC organised a collaborative trial at European level with the participation of 17 European laboratories. The validation exercise was conducted and evaluated according to ISO 5725:1994 (parts 1, 2 and 6). The first aim of the study was the validation of the *d* correction factors for PAC using methods 2, 8 and 11 of Directive 96/73/EC. The second aim was the validation of method 11 as quantitative method for binary mixtures PA/PAC, including the determination of the method's accuracy in terms of trueness and precision.

The initial plan was to use samples of both PAC 20 % and 40 % in the validation exercise; however, PAC 40 % (samples **266** and **281**) newly produced by Aquafil showed solubility properties completely different from the ones of sample **199** (Table 51). In fact, the producer was unable to reproduce PAC 40 % which remains insoluble when treated with method 11, as it was the case for sample **199**. For this reason PAC 40 % was finally not included in the collaborative study.

Table 51: Solubility properties of PAC 40 % (method 11).

JRC code	replicates	insoluble component %	conf. limit (95%)	*d*	conf. limit (95%)
199	10	96.93	0.15	**1.032**	0.16
266	5	65.51	1.14	**1.518**	1.11
281	3	82.52	6.92	**1.230**	6.95

For the validation of the *d* values, yarns of PAC 20 % (sample **280**), provided by the petitioner, were used. For the validation of method 11, a balanced uniform level test was performed. Carpet samples made of binary mixtures PA/PAC 20 % of three levels of concentration (PA content about 25, 50 and 75 %) were sent to participants (samples **282 - 284**). Loop twisted carpets were chosen in order to be able to obtain reference values through quantification done *via* manual separation. Each laboratory analysed five replicates for every sample under repeatability conditions.

6.1 Design of the collaborative trial

Seventeen laboratories from fifteen EU member states (BE, CZ, FI, FR, DE, EL, HU, IT, LT, PL, PT, RO, SK, ES and UK), members of the ENNETL, participated in the validation study. The participants were provided with test samples, instruction guidelines and an electronic reporting sheet containing formulas to collect results. They were requested to strictly follow the protocols of methods 2 and 8, as described in Directive 96/73/EC. On the contrary, in the case of method 11 a slight modification in the procedure was adopted. Work conducted by the JRC had shown that, in case method 11 would have to be used for binary mixtures containing the new fibre and polyamide in concentration higher than 60 %, accurate quantification could only be achieved modifying the washing procedure. For this reason, participants were asked to apply the modified version of method 11. The modification foresaw the addition of two new washing steps of PAC residue with 75 % sulfuric acid solution before applying the normal washing procedure.

6.2 Homogeneity study

For the validation study, in the case of yarns, the fibre had to be homogenised before being sent to participants. Homogenisation was performed using a glass round-bottom balloon of 50 l capacity. Due to the big quantity of homogenised sample needed, the yarn sample was divided into five batches of about 70 g each, for every method. Fibres of every batch were cut into pieces of about 10 mm and inserted into the balloon. The balloon was tapped with an elastic porous tissue, through which compressed air was applied for 5 minutes to mix the fibres, using an air blow gun. From each homogenised batch a testing specimen of about 2.6 g was packed in a plastic package. Half of the quantity of each testing specimen (about 1.3 g) had to be analysed under repeatability conditions for the determination of the *d* correction factor. The second halves had to be considered as spare samples, to be analysed only in case of errors during the quantification of one or more testing specimens. In that case, all five spare specimens had to be quantified together under repeatability conditions.

In the case of carpets, five batches were selected longitudinally from each of the three carpet samples. Every batch was sub-divided into 24 testing specimens of 2.6 g each.

Each testing specimen was split in two pieces of 1.3 g each, placed together in the same aluminium foil package. Again, only one piece of each specimen (1.3 g) had to be quantified in repeatability conditions and the rest had to be considered as a spare sample.

Homogeneity tests were performed according to the accepted procedure of the test for 'sufficient homogeneity' [7]. For yarn sample **280**, two testing specimens of 2.6 g each were randomly selected from the homogenised batches (five for every method) and analysed in duplicate with methods 2, 8 and 11. The 20 replicates (for each method) were analysed under randomised repeatability conditions. All results were checked for outliers according to Cochran's test and were retained as there was no evidence for analytical outliers. The statistical evaluation of results showed that the yarn sample was 'sufficiently homogeneous' when tested with methods 2, 8 and 11 and that there was no evidence for significant differences among the five batches.

For every carpet (samples **282 - 284**), two testing specimens of 2.6 g each were randomly selected from each of the five batches and analysed in duplicate with method 11. Analyses on the 20 replicates, carried out under randomised repeatability conditions, showed that there was no evidence for analytical outliers according to Cochran's test. As in the case of yarn sample, the statistical evaluation of results showed that carpet samples could be considered 'sufficiently homogeneous' when tested with method 11 and that there was no evidence for significant differences among the five batches.

Consequently, both yarn and carpet samples were considered suitable to be sent to participants for the purposes of the validation study. For each sample and method, five testing specimens were randomly provided to every laboratory participant, one from each batch.

6.3 Results of collaborative trial

All participant laboratories reported results. At first, data were investigated for outliers according to Mandel's *h* parameters to detect laboratories with high or low extreme mean values and according to Mandel's *k* parameters to detect laboratories with poor repeatability. No decision about possible elimination of suspect data was taken on the basis of Mandel's statistics. Secondly, Cochran's and Grubbs' tests were carried out to identify numerical outliers. Based on these tests, data considered

outliers were eliminated, whereas data considered stragglers were retained. Repeatability and reproducibility standard deviations were calculated according to ISO 5725-2 in order to obtain the repeatability and reproducibility limits (r and R, respectively).
In the case of the evaluation of *d* correction factors, for the calculation of the precision parameters, according to Cochran's test one outlier was rejected for method 2 and two for method 11. Final results were:

Method 2	$d = 1.001$	r = 0.0031	R = 0.0077
Method 8	$d = 1.004$	r = 0.0047	R = 0.0146
Method 11	$d = 1.005$	r = 0.0039	R = 0.0089

In the case of the validation of method 11 for the quantification of binary mixtures PA/PAC, for the calculation of the precision parameters, two outliers were eliminated according to Grubbs for the carpet sample **284** (approximate concentration of PAC 75 %).
The trueness of the method (expressed as bias) was calculated, for the three levels of concentration, as the difference between the content of PAC (%), obtained by method 11, and its reference value, obtained by manual separation. Manual separation was performed on ten replicates, two from each of the five batches from which testing specimens were sent to participants. The bias of the method, calculated using a *d* factor value equal to 1.005, was in the range 0.06 – 0.48 %, increasing with the content of polyamide. Using four levels of concentration (the three carpet samples plus the PAC 20 % yarn analysed to establish *d*), a linear relationship was found between bias and % PAC.
The *d* value for PAC in method 11, determined through the collaborative trial, was 1.005; however, *d* correction factors in Directive 96/73/EC are usually reported with two decimals. For this reason, the influence of the *d* factor on trueness was evaluated using the three values 1.00, 1.005 and 1.01. Following ISO 5725-6, critical differences were calculated using these three values. Best results were obtained in the case of $d = 1.005$, where the bias could be considered acceptable in three out of four levels of concentration. Therefore, this value was proposed by the JRC.
Results regarding precision parameters, calculated using *d* factor equal to 1.005, were:

PAC % = 76.96	r (%) = 0.69	R (%) = 0.97	bias (%) = 0.06
PAC % = 48.43	r (%) = 1.04	R (%) = 1.87	bias (%) = 0.28
PAC % = 27.35	r (%) = 0.95	R (%) = 1.68	bias (%) = 0.48

On this basis, the JRC proposed the value of 2 %, as the reproducibility limit of method 11, to be inserted in Directive 96/73/EC.

7. 11th ENNETL meeting

As discussed during the 9th and 10th ENNETL meetings, experts confirmed that, in their point of view, the term “composite” should not be part neither of the name nor of the definition of the new fibre. They were, instead, in favour of the term “bicomponent” fibre. Moreover, they were of the opinion that the term “propylamide”, proposed by the petitioner, could mislead giving wrong idea about the chemical composition of the fibre. “Bi-polypropylene/polyamide” and “polypropylene/polyamide bicomponent” were considered good proposals for the following reasons: first of all, the names of constituents are stated and secondly, both bi- and bicomponent introduce the idea of a multicomponent fibre. A written consultation of national experts was organised by the JRC and the name preferred by the majority was “*polypropylene/polyamide bicomponent*”.

Regarding the definition, as far as the range of composition is concerned, experts decided to change the proposed range 10 % - 45 %, due to the problems experienced with PAC 40 %. In fact, solubility properties of different samples of PAC 40 % were proved to be substantially different, thus strongly influencing their behaviour when method 11 was applied (see chapter 6). The group of experts judged that an analytical method to quantify binary mixtures PA/PAC is needed to allow market surveillance and, for this reason, they agreed to restrict the range of composition to 10 % – 25 %. Some experts were of the opinion that the structure “islands-in-the-sea” should be mentioned in the definition and questioned the term “fibrils”. On the basis of a written consultation regarding the new definition in its various possible forms, the majority of experts chose the following: “*a bicomponent fibre composed of between 10 % and 25 % by mass of polyamide fibrils embedded in polypropylene matrix*”.

Experts agreed on the adoption of 1.00 %, as the value of *agreed allowance* for the new fibre (see par. 5.3), based on the restriction of composition’s range for PAC (10 % – 25 %) and on the average result (about 0.40 %). According to experimental results, experts agreed on the value of 0 % as the *b* correction factor for mass loss due to pre-treatment (see par. 5.2).

The group agreed that, according to the results of the validation study, the field of application of method 11 shall be extended to binary mixtures PA/PAC and the following *d* factor values for PAC should be inserted in Directive 96/73/EC: 1.00 for methods 2 and 8 and 1.005 for method 11. They also considered necessary to be specified that, in the description of method 11 for binary mixtures PA/PAC, the modified washing procedure has to be followed and the reproducibility limit is 2 %.

In addition, they were of the opinion that all the other *d* correction factors evaluated by the JRC both for PAC and PP shall be trusted and inserted in Directive 96/73/EC on the basis of 20 replicates.

8. Further experimental work

As the experimental work performed on solubility properties had been essentially done on PAC 40 % and due to the decision of restricting the composition's range for the new fibre (10 % – 25 %), further experimental work was conducted by the JRC on PAC 20 %. Twenty replicates were analysed in case PAC resulted to be insoluble, in order to establish the *d* correction factors. Analyses on ten replicates were performed in case PAC was partially soluble.

Table 52: Solubility properties of PAC 20 %.

JRC code	method	replicates	insoluble component %	conf.limit (95%)	*d*	conf.limit (95%)
233	**1**	19	99.83	0.094	**1.002**	0.001
233	**3**	10	82.23	0.148	**partially soluble**	-
233	**4**	10	94.60	0.301	**partially soluble**	-
233	**5**	20	100.25	0.258	**0.997**	0.003
233	**6**	20	99.84	0.082	**1.002**	0.001
233	**7**	20	99.38	0.048	**1.006**	0.001
233	**9**	19	99.90	0.106	**1.001**	0.001
233	**10**	20	99.92	0.093	**1.001**	0.001
233	**14**	20	99.30	0.095	**1.007**	0.001

As shown in Table 52, PAC 20 % was proven to be partially soluble under the conditions of methods 3 and 4 and insoluble in methods 1, 5-7, 9, 10 and 14. The *d* correction factor values were 1.00 for methods 1, 5, 6, 9 and 10, whereas methods 7 and 14 showed *d* values equal to 1.01.

9. Conclusions

On the basis of experimental results, discussions during the 9th, 10th and 11th ENNETL meetings (20th October 2008, 10th December 2009 and 15th July 2010) and written consultation with national experts, the name and definition agreed and proposed for the new fibre are "*polypropylene/polyamide bicomponent: a bicomponent fibre composed of between 10 % and 25 % by mass of polyamide fibrils embedded in polypropylene matrix*".

Experimental work conducted at the JRC confirmed that test methods are available for the identification and quantification of the new fibre PAC.

As far as the identification methods are concerned, experts agreed with the JRC that Scanning Electronic Microscope (SEM) analysis is an adequate method, whereas optical microscopy is not. Additionally, Fourier Transform Infrared Spectroscopy (FT-IR) and Differential Scanning Calorimetry (DSC) can be used as techniques to differentiate PAC from binary mixtures PP - PA.

For quantification purposes, the normal pre-treatment described in Directive 96/73/EC, was proved to be applicable to the new fibre. Ventilated oven can be used, instead of the vacuum one proposed by the applicant, as statistical evaluation showed that results could be considered equivalent in the two cases. The *agreed allowance* of the new fibre and the correction factor *b* for mass loss during pre-treatment were experimentally evaluated. The resulting values, adopted by the network of national experts from member states, were 1.00 % and 0 % respectively. Additionally, the solubility properties of the new fibre were evaluated with all methods described in Directive 96/73/EC. The solubility behaviour of PA6 and PP was studied as well, in case the information is not included in Directive 96/73/EC.

The new fibre was proved to be insoluble in methods 1, 2, 5-11 and 14. The *d* correction factors were established on the basis of the experimental work carried out by the JRC and, in the case of methods 2, 8 and 11, checked through a collaborative trial at European level. For the determination of the *d* correction values, yarns of pure PAC 20 % were used. The resulting values were: 1.00 for methods 1, 2, 5, 6, 8-10, 1.005 for method 11 and 1.01 for methods 7 and 14.

Polypropylene was insoluble in methods 1, 3, 5-11, 14 and 16; the average *d* factor values were 1.00 in all cases. Polyamide 6 was shown to be insoluble in methods 5 and 10 and the average *d* factor values were 1.00 and 1.01, respectively. Experts agreed that only the correction factors *d* for PAC and PP shall be inserted in Directive 96/73/EC, as the ones for polyamide were measured just on PA6.

The JRC examined the applicability and evaluated the accuracy of the three methods (hydrolysis, DSC and FTIR) proposed by the petitioner to quantify the content of PA in PAC. In addition, a series of chemical dissolution methods were investigated in the attempt to find accurate and less time-consuming alternative methods for this quantification. PA6 in PAC was quantified *via* elemental analysis on the basis of the nitrogen content of PAC samples, which is only due to the polyamide component. Results obtained with this technique were considered reference values against which all other results were compared.

The DSC and FT-IR methods quantified accurately PA6 in PAC, but showed the disadvantage to require the availability of standards of PAC of various PA contents in order to build up calibration curves. The hydrolysis method, apart from the fact that it was very time-consuming, did not present results similar to the reference values. Among the chemical dissolution methods tested, method 16 of Directive 96/73/EC was proved to be in good agreement with elemental analysis. Therefore, it was proposed by the JRC and agreed by national experts as the most suitable method for the quantification of the PA6 content of the new fibre.

For the quantification of PAC in binary mixtures with PA and PP, manual separation is an adequate technique whenever feasible. Alternatively, several methods were investigated not only on yarns but also on real carpet samples. The accuracy of these methods was evaluated by comparing quantification results to the ones obtained *via* manual separation on twisted yarns. The DSC method, proposed by the petitioner, resulted to be not accurate, neither in the case of mixtures PA/PAC nor of PP/PAC.

For the quantification of binary mixtures PA/PAC, method 11 of Directive 96/73/EC was judged very accurate, as results were in very good agreement with the reference values. In fact, 75 % sulphuric acid solution at room temperature (1 h contact time) was able to solubilise only the PA fibres in the binary mixture and not the PA fibrils inside PAC. For the quantification of binary mixtures PP/PAC, method 16 of Directive 96/73/EC was proved to be accurate when compared to the reference values. PA inside PAC could be solubilised using 90 % formic acid at 90 ^{o}C (1 h contact time). However, the great disadvantage that the PA content of PAC should be known for the calculation of results cannot be neglected. In an attempt to overcome this problem, a densitometric approach was used to separate PAC from PP/PAC binary mixtures, to allow the quantification of PA content in it; however, several problems were experienced leading to lack of repeatability.

On the basis of experimental results obtained also on real carpet samples, the JRC proposed method 11 as the adequate one for quantifying mixtures PA/PAC. During the 10th ENNETL meeting, a consensus was reached on the need to validate method 11 to extend the field of application to this binary mixture. Consequently, the JRC organised a successful collaborative trial with the participation of 17 European laboratories, in accordance with the rules laid down in ISO 5725:1994. For the validation of method 11, a balanced uniform level test was performed. Loop twisted carpet samples made of binary mixtures PA/PAC 20 % of three levels of concentration (PA content around 25, 50 and 75 %) were tested for sufficient homogeneity and sent to participants. Carpet samples were quantified also *via* manual separation in order to obtain reference values against which compare results.

Based on the outcome of the validation study, experts agreed that the field of application of method 11 shall be extended to the quantification of binary mixtures PA/PAC. The JRC and experts were of the opinion that, in the description of method 11, the reproducibility limit of 2 % shall be specified in the case of binary mixtures PA/PAC. Furthermore, it was decided that the modified washing procedure, used in the collaborative study and needed to obtain correct quantification of mixtures PA/PAC with high percentages of PA fibres, must be inserted in Directive 96/73/EC.

10. References

[1] Directive 96/74/EC of the European Parliament and of the Council of 16 December 1996 on textile names *(Official Journal L032 of 3.2.1997 p. 0038-0055)*.

[2] Directive 2008/121/EC of the European Parliament and of the Council of 14 January 2009 on textile names (recast) *(Official Journal L019 of 23.1.2009 p. 0029-0048)*.

[3] Directive 96/73/EC of the European Parliament and of the Council of 16 December 1996 on certain methods for the quantitative analysis of binary textile fibre mixtures *(Official Journal L032 of 3.2.1997 p. 0001-0037)*.

[4] ISO 6348 (1980). Textiles. Determination of mass. Vocabulary. International Organization for Standardization, Geneva, Switzerland

[5] ISO 5725 (1994). Accuracy (trueness and precision) of measurement methods and results. International Organization for Standardization, Geneva, Switzerland.

[6] Miller, J. N., Miller, J. C., Statistics and Chemometrics for Analytical Chemistry. Pearson Education Limited, .5th Ed, 2005.

[7] Thompson, M., Ellison, S. L. R., Wood, R., The international harmonized protocol for the proficiency testing of analytical chemistry laboratories (IUPAC Technical Report), *Pure Appl. Chem.*, 2006, **78 (1)**, 145.

Annex I

Analytical methods proposed by the applicant

Development of Experimental Methodologies for the Identification of the PAC fibre in commercial fibre blends.

Summary.

Aquafil applied for a New Generic Name on November the 8th 2005 and presented the new fibre to the Commission of the Member States Technical Experts W.G. on Textile Labelling on the 6th of February 2006 . The new fibre is based on a chemical blend of PA and PP, whereas the PA is shaped in a nanofibrils form inside the PP matrix.

The proposed Fibre definition was: 'A composite fibre composed of between 10% and 45% by mass of polyamide fibrils embedded in polypropylene matrix' and the proposed Generic Name was Propylamidecomposite (PAC). In this report this will be used.

Following the positive discussion and decision made by the EU Commission W.G., a request was issued by the same Commission to Aquafil to propose specific methodologies for the quantitative identification of the new fibre inside fibres blends.

Activities done by Aquafil, also in collaboration with the University of Trento, were concentrated on the PA/PP/PAC blends, as, in case of other blends other known and simple analysis, will provide the information.

Results indicate that it is possible to discriminate and measure the quantity of the new fibre inside a fibre blends, both binary and ternary. In particular the chemical elimination of the PA part seems to be particularly useful in case of mixtures with PA fibres, while the fibre differentiation through density separation can be proposed as a general method for any type of fibre blend.

Sample preparation.

Fibre blends were prepared by air-entangling of different BCF yarns, as listed in Tab.1. This reprocessing technology is characterised by the physical intimate mixing of the singles filaments of each yarn and physical knots are created. The actual Wt% for each fibre was calculated from original yarn's denier. It must be remarked that the error in the dtex measurement is about ±1,5% and therefore the minimum wt% error in the real quantity of fibre present can be estimated to be about ±1%.

Tab.1 – List of fibre blends prepared for the methodology evaluation.

	1	2	3	4	5	6	7
	wt.%	wt.%	wt.%	wt.%	wt.%	wt.%	wt.%
PAC	48,5	55	35			77	36
PA	50,5		37	74			30
PP		45	28		65		22
PES				26	35	23	12

Qualitative and Quantitative fibre determination inside fibre blends

A) Colorimetric Fibre Identification.

This method is based on the fact that the different polymers do have a different chemical behaviour towards dyestuffs. In particular: PA 6 and 66 shows a chemical reaction against acid and/or cationic dyestuffs, while PAC or PES does not.

Methodology description.

1. Fibre preparation with spin finish removal using petrol ether or methyl alcohol and drying for 2 h at 100°C.
2. Fibre weighing.
3. Liquor preparation using following dyestuff types and concentrations:
   a. 1% acid + 1% cationic for PA/PAC blends
   b. 1% disperse for PAC/PP blends
4. Dyeing conditions: 60°C for 5 min, pH 6, liquor ratio: 40 g bath each g of fibre
5. Fibre washing: 50°C for 5 min and drying at 100°C for 2 h.
6. Fibre separation by hand
7. Fibre weighing.

Methodology application

Fig.1 shows the colour differentiation evident in the case of the PA/PAC (acid dyestuff Tectilon Blue+ cationic Maxilon Blu) blend, for the PP/PA/PAC blend (acid Tectilon Blue+ cationic Maxilon Blu + disperse dyestuff Dianix Red) and for the PP/PAC blend (disperse dyestuff Dianix Red) in case of rope dyeing). Results are given in Tab.2.

Fig.1 – Colour differentiation for PAC fibre blended with PP and PA fibres.

Tab.2 – PAC quantity measurement achieved using the colorimetric method

	PAC wt% content	PAC wt% measured
PAC + PP	55	53
PAC +PA6	48,5	49
PAC +PA6+PP	35	33,5

Comments on the methodology proposed.

The proposed method is very easy in case of PAC / PA blends . Hand separation could be more difficult in case of dark dyed fibres (less colour contrast) and very short fibres.

The precision of the method is linked to the precision of fibre separation.

In the case of carpets, dying can be done directly on it before pile cutting.

This method could be used un conjunction with other methods, e.g. with the physical separation by density, to have a cross-check the nature of the fibre.

B) Chemical dissolution of PA

This method is valid for PA/PAC fibres or PA/PP/PAC. It is based on the different chemical reaction of the fibres towards chemicals. In particular, PA fibres are dissolved by acids, like formic acid, while PAC does not.

Methodology Description.

1. Preparation of 1 g of yarn inside a bottle of 150 ml
2. Spin finish removal using petrol ether or methyl alcohol and drying for 2 h at 100°C
3. Introduction of 100 ml of formic acid solution with 70% concentration at 25°C for 10 min.
4. Removal of the formic acid and fibre washing using distilled water
5. Fibre drying at 100°C for 5 h
6. Fibre weighing and ratio calculation

Methodology application and testing

PAC/PA6 (sample n.1), PAC/PP (sample n.2) and PAC/PA6/PP (sample n.3) fibres were tested using different acid formic concentrations. Moreover, to understand the possible error of the methodology proposed, the same was applied on 100% PA6 fibre, 100% PP fibres

Finally also 100% PAC fibre, produced with a PA6 nano-fibrils content in the range 10 - 35%, and different 100%PAC fibres engineered with a 20% PA6 nano-fibrils, were tested to evaluate the error induced by the different fibre engineering, using the best formic acid solution.

Table 3 compare the results achieved, i.e. the quantity of PA removed, with real PA content.

Tab.3 – Results of chemical removal of PA fibre in various blend using different formic acid solution concentrations

	PA% content	PA% measured		
		Formic Acid concentration		
		50%	70%	80%
PP	0	0	0	0,0
PA6	100	2,47	100	100
PAC	0	0,34	0,42	1,21
PAC + PP	0	0,7	0,4	0,9
PAC +PA6	51,1	1	51,8	52,5
PAC +PA6+PP	36,9	1	37,2	38,1

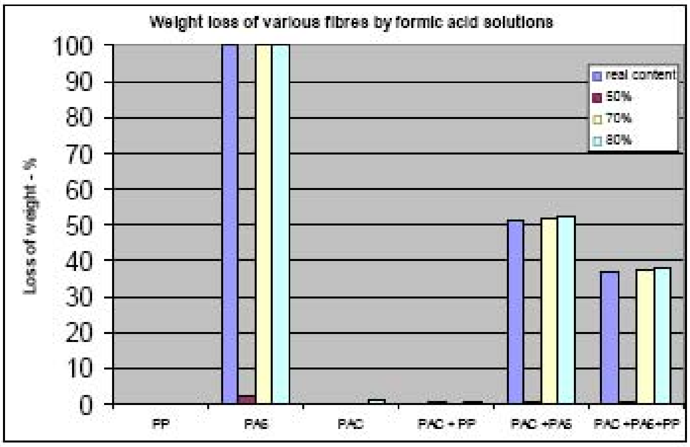


Fig.2 – Results of chemical removal of PA fibre in various blend using different formic acid solution concentrations

Results on pure PAC fibre indicate that a systematic error of about 0,4 can be present with concentration of 70% formic acid, while using 50% concentration time is not sufficient even to solve the pure PA6 fibre.

The effect of the concentration of PA6 nano-fibrils inside the PAC fibre on data reliability, tested using the 70% of formic acid solution concentration, is listed in Tab.4, that shows that the systematic error is increased by increasing the amount of PA6 nanofibrils concentration, up to a 1,2% value.

Tab.4 – Effect of the PP/PA ratio of the PAC fibre on test precision.

Fibre Type	% PA6
PAC - 10% PA6	0,2
PAC - 15% PA6	0,25
PAC - 20% PA6 - A	0,42
PAC - 20% PA6 - B	0,4
PAC - 20% PA6 - C	0,55
PAC - 35% PA6	1,29

Comments on the methodology proposed.

The methodology, seems to be useful to discriminate the presence of PA from the one of PAC. It can be easily used on carpet, as carpet pile can be cut with a razor blade and do not have the problem of fibre hand-separation. Do not require complicated instrumentations.

The systematic error, the overestimation of the PA fibre content, is proportional to the PAC wt% present. Therefore, supposing that an error of 1,2wt% of weight loss is measured on 100% PAC fibre, an error of 0,6wt% will result of blends 50wt%PAC / 50wt%PA6 (0,3% difference in the real PA6 quantity present), which seems to be tolerable.

C) Physical separation of the fibres.

The method proposed is valid for the most part of synthetic fibres. Is based on the fact that different polymers do have a different density. Tab.5 lists the most common polymers together with their density range, while Fig.3 shows the measured density range for different types of the PAC fibre family.

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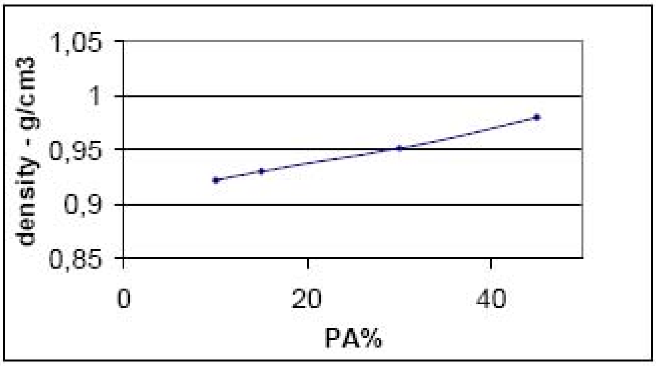


Fig.3 – Density range for the PAC fibre as a function of the nanofibrils content.

Tab.5 – Density range for different synthetic fibres.

	density min	(g/cm3) max
PET	1,36	1,38
PA	1,12	1,14
PAC	0,93	0,98
PP	0,89	0,905

Density separation can be easily done using specific water solutions:

- if the fibre density is higher than the one of the solution she will sink down,
- if her density is lower, she will remain on the solution surface.

To separate to fibres having a different density a solution characterised by an intermediate density must be chosen. Following water solutions are proposed:

The solutions proposed and tested are the following:

i. Distilled water – 1 g/cm3
ii. Distilled water saturated with NaCl – 1,19 g/cm3
iii. Distilled water with 50% of Ethylic Alcohol – 0,93 g/cm3

A) Distilled Water

The density of pure, distilled water is around 1 g/cm3, as indicated by Tab.6

Tab.6 – Density values of distilled water as a function of temperature.

19°C	20°C	21°C	22°C	23°C	24°C
0,9984 g/cm³	0,9982 g/cm³	0,9980 g/cm³	0,9978 g/cm³	0,9975 g/cm³	0,9973 g/cm³
25°C	26°C	27°C	28°C	29°C	30°C
0,9970 g/cm³	0,9968 g/cm³	0,9965 g/cm³	0,9962 g/cm³	0,9959 g/cm³	0,9956 g/cm³

B) Saturated NaCl water solution

NaCl maximum solubility limit is about 26wt% (358g/l). Under those stable conditions (an excess of NaCl will precipitate), the solution density is around 1,19, as predicted from Tab.7:

Tab.7 – Density values of saturated NaCl water solution as a function of temperature.

19°C	20°C	21°C	22°C	23°C	24°C
1,1952 g/cm³	1,1946 g/cm³	1,194 g/cm³	1,1934 g/cm³	1,1928 g/cm³	1,1922 g/cm³
25°C	26°C	27°C	28°C	29°C	30°C
1,192 g/cm³	1,1911 g/cm³	1,1905 g/cm³	1,1899 g/cm³	1,1893 g/cm³	1,1888 g/cm³

C) Ethanol - water solution
Fig.4 shows the density of ethanol-water solutions: to achieve a density of about 0,926 g/cm3 , required to separate the PP from the PAC fibres, a solution of water with 50wt% of Ethylic Alcohol (commercial product with 95% concentration) is needed. Tab.8 shows also the correction factor as a function of temperature.

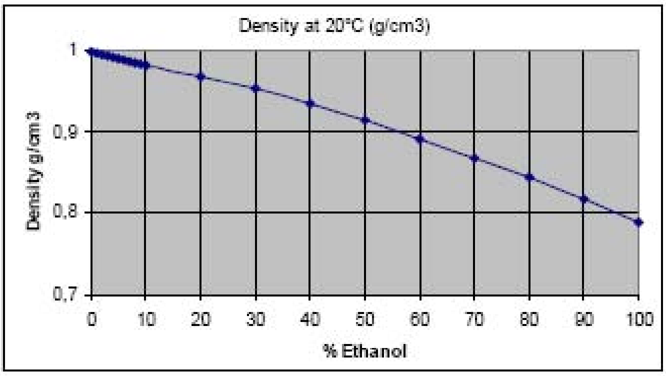


Fig.4 – Density values of ethanol - water solution

Tab.8 – Ethanol quantity correction required as function of the temperature to achieve a density value of 0,926 g/cm3

19°C	20°C	21°C	22°C	23°C	24°C
50,9%	50,6%	50,3%	50%	49,8%	49,5%
25°C	26°C	27°C	28°C	29°C	30°C
49,2%	48,9%	48,6%	48,4%	48,1%	47,8%

To evaluate a possible effect of alcohol evaporation on density, the stability of the solution in time was analysed. Results as a function of time are reported in following Fig.5. Results are consistent with literature (Perry's Chemical Engineers' Hand Book – Seventh Edition- Robert H.Perry, Don W. Green – pag. 2-112).

It is important to remark that an exothermic reaction is occurring during the first 1-2 days, as the peak is showing, with the formation of air bubbles. Those air bubbles can be trapped by the single filaments and drive then towards the surface of the bottle, therefore introducing an error in the quantitative measurement. It must be concluded that the solution has to be prepared al least 2 days before the measurement. Moreover the use of some surfactant (e.g. some droplets of liquid soap) can be beneficial and are suggested in removing the air bubbles form single filament's surface.

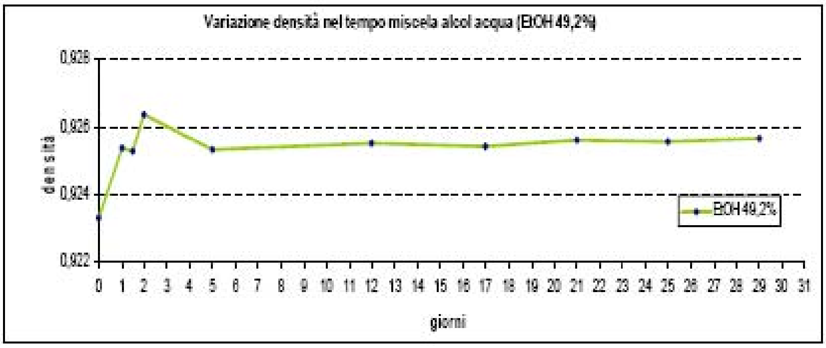


Fig.5 – Experimental time dependent of the density of Ethanol – Water solution. The first peak seems to be related to an exothermic reaction whereas the formation of air bubbles was visible

<u>Methodology Description.</u>

1. Yarn cut – single filaments must be no longer than 5mm, entangling knots or other bonding points must be removed, single filaments must be physically separated
2. Preparation of 50 g of yarn inside a bottle of 500 ml
3. Spin finish removal using petrol ether or methyl alcohol and drying for 2 h at 100°C
4. Introduction of the water solution, prepared at least 2 days before, selected as a function of the fibre mixture to be analysed:
    - distilled water for PAC/PES or PAC/PA;
    - NaCl saturated water for PAC/PES
    - water/ethylic alcohol for PAC/PP mixtures.
5. Mixing of the fibre inside the solution until all have been are wetted and have been separated one from the other. If some bundle of fibres are formed, they have to be removed and their weight subtracted from the total sample weight.

6. After more than 24 h, separation of the fibres that are emerging from the one that are sunk down using a filter or other separation methods
7. Fibres rinsing with distilled water and drying at 100°C for 1 h
8. Fibre weight measurement

The selection of the right solution for the separation of the single fibres is indicated in Tab.9.

Tab.9 – Solution selection for each binary and ternary fibre mixture used in this study and fibre behaviour - W=Distilled Water; SW=NaCl Salt Water; W/EA=Ethanol/ Water

--------	PET	PA6	PAC	PP	PET + PA6	PAC + PP
PET	--------	SW PET down PA6 up	W PET down MTX up	W PET down PP up	--------	W PET down MTX+PP gup.
PA6	W/S PET down PA6 up	--------	W PA6 down MTX up	W PA6 down PP up	--------	W PA6 down MTX+PP gup.
PAC	W PET down MTX up	W PA6 down MTX up	--------	W/EA MTX down PP up	W PET+PA6 down MTX up	--------
PP	W PET down PP up	W PA6 down PP up	W/EA MTX down PP up	--------	W PET+PA6 down PP up	--------
PET + PA6	--------	--------	W PET+PA6 down MTX up	W PET+PA6 down PP up	--------	W PET+PA6 down MTX+PP gup
MTX + PP	W PET down MTX+PP gup	W PA6 down MTX+PP gup.	--------	--------	W PET+PA6 down MTX+PP gup	--------

Methodology application and testing

This methodology was applied on all samples listed in Tab.1, i.e. on binary and ternary PAC blends with PP, PA, PES. In Fig. 6 the fibre preparation is shown, while Fig.7 shows the fibre separation inside the bottle.

Experimental results are summarised in Tab.10, together with the set fibre quantity.

Fig.6 – Fibre preparation for the physical separation

Fig.7 – PAC / PP fibre separation inside the bottle

Tab.10 – Results of quantitative measurement of different fibre blends by means of the physical fibre separation using the proposed methodology on all sample. The set value is also indicated for comparison purposes.

	1		2		3		4		5		6		7	
	set wt.%	result	set wt.%	result	set wt.%	measured	set wt.%	result	set wt.%	result	set wt.%	result	set wt.%	result
PAC	48,5	47,8	55	54,2	35	34,8					77	76,8	36	36,9
PA	50,5	52,2			37	35,7	74	73,4					30	29,7
PP			45	45,8	28	29,5			65	64,1			22	22,6
PES							26	26,5	35	35,9	23	23,2	12	10,8

MISURA DELLA % DI NYLON NELLA FIBRA PAC TRAMITE FTIR CON ACCESSORIO ATR

1. SCOPO

Scopo di questo metodo è la determinazione della quantità di nylon presente nella fibra di PAC

2. PRINCIPIO DEL METODO

La metodologia utilizzata prevede l'analisi della trasmittanza % a determinate lunghezze d'onda specifiche del nylon e del polipropilene nella fibra PAC

3. REAGENTI OCCORRENTI

- Alcool Metilico RP

4. MATERIALE OCCORRENTE

- Pallone da 250 ml

5. APPARECCHIATURA OCCORRENTE

- Stufa sotto vuoto
- Spettrofotometro FTIR Spectum 100 Perkin Elmer con modulo ATR

6.PROCEDIMENTO

- Lavare a freddo una matassina da 2 g circa con alcool metilico
- Asciugare in stufa sotto vuoto a 50°c per almeno 1 ora e comunque fino a peso costante
- Acquisire uno spettro FTIR del campione eseguendo una scansione nel range 4000 a 650 cm^{-1}, risoluzione 4cm^{-1} e 16 accumulazioni.

7. ANALISI DELLO SPETTRO OTTENUTO

Procedura manuale:

Diagrammare lo spettro in assorbanza

- Identificare i picchi caratteristici delle fasi PA6 e PP nella fibra PAC:
  - Picco 1 presso 1650 cm^{-1} assegnato alla poliammide (ammide I)
  - Picco 2 presso 1450 cm^{-1} assegnato al polipropilene (CH3 bending)
- Integrare i picchi identificati al punto precedente utilizzando i seguenti estremi di integrazione e le base-line lineari corrispondenti
  - Picco 1: da 1700 a 1595 cm^{-1} con base-line da 1700 a 1595 cm^{-1}
  - Picco 2: da 1500 a 1400 cm^{-1} con base-line da 1500 a 1400 cm^{-1}
- Calcolare il rapporto delle aree dei picchi 1 e 2 precedentemente ottenuti: $R_{exp} = A_{picco1} / A_{picco2}$
- Utilizzare la seguente formula per il calcolo della percentuale di PA6 totale nella fibra PAC:
  $PA6\% = 0.312 + 10.146 {*} R_{exp}$

Procedura automatica (software Perkin Elmer)

- Dopo aver acquisito lo spettro sottrarre una base-line rettilinea che interechi la curva di trasmittanza dello spettro a 2155 cm^{-1}.
- Applicare il metodo Quant®, richiamando il file di calibrazione PAC_1450, allo spettro così ottenuto.
- La percentuale di PA6 totale nella fibra PAC analizzata è fornita dal report automatico generato dal metodo.

8. COSTRUZIONE CURVA DI TARATURA

DATA: 22/11/07 PREPARATO : ...Paralovo............................ APPROVATO : ....
DESCRIZIONE MODIFICA : ....

IDROLISI NYLON NELLA FIBRA PAC

1. SCOPO
Scopo di questo metodo è la determinazione della quantità di nylon presente nella fibra di PAC

2. PRINCIPIO DEL METODO
Una piccola quantità di campione viene idrolizzata a caldo a riflusso per 16 ore con acido cloridrico al 37% diluito 1:1 , in questo modo si idrolizza completamente la componente nylon della fibra , quindi sottraendo al peso iniziale, la fibra rimasta dopo l'idrolisi, posso risalire alla composizione in % di nylon.

3. REAGENTI OCCORRENTI
- Acido Cloridrico al 37%
- Acido Cloridrico 1:1
- Etere di petrolio 40°-60° RP
- Alcool etilico RP
- Alcool metilico RP

4. MATERIALE OCCORRENTE
- Pallone da 250 ml
- refrigerante
- calotta riscaldante
- Soxhlet

5. APPARECCHIATURA OCCORRENTE
- Stufa
- Stufa sotto vuoto
- bilancia analitica precisione 0.0001

6.PROCEDIMENTO
- Pesare circa 1 grammo di campione in un pesafiltro di ppl
- Introdurlo in estrattore Soxhlet da 100 ml
- Aggiungere 150 ml di etere di petrolio
- Estrarre il tutto in Soxhlet per 1 ora o per 6 cicli per estrarre l'olio di ensimaggio dalla fibra
- Recuperare la fibra lavata con etere porla in un pesafiltro introducendo il tutto in stufa a 105°C per 5 ore e pesare infine la fibra a peso costante
- Introdurre la fibra lavata e asciugata in un pallone da 250 ml e aggiungere 100 ml di acido cloridrico 1:1
- Riscaldare il tutto al bollo a riflusso per 16 ore
- Recuperare la fibra dopo le 16 ore di idrolisi lavandola con acqua in un complesso filtrante sotto vuoto fino a che le acque di lavaggio non risultano completamente neutre PH 7-7.5
- Lavare infine la fibra con alcool metilico a caldo ,circa 100 ml, e porla ad asciugare per quattro ore ,comunque fino a completo asciugamento,in stufa a 105°C per almeno 5 ore in ogni caso fino a peso costante

7.CALCOLI

- Pesare la fibra lavata ed eseguire il seguente calcolo:

$$\% \text{ nylon} = (P1 - P2) / P1 \times 100$$

dove : P1= peso fibra dopo lavaggio con etere e asciugamento
P2= peso fibra dopo idrolisi lavaggio e asciugamento

DATA: 22/11/07 PREPARATO : ...Paralovo.......................... APPROVATO : ....
DESCRIZIONE MODIFICA : ....

Metodi di identificazione fibre PAC (PP/PA6)

Misura della percentuale di Nylon nelle fibre PAC

Misura della percentuale di PAC in fibre in mista

Arco (TN) 03/04/2007

Indice

1. Introduzione

Nelle precedenti relazioni si era cercato di mettere a punto delle metodologie adatte per l'identificazione della percentuale di Nylon in fibre PAC e della percentuale di fibra PAC in miste. In particolare si era visto che per l'individuazione della percentuale di Nylon in fibre PAC possono essere utilizzate le seguenti analisi:

- Idrolisi del Nylon in acido cloridrico;
- Attacco acido del Nylon in acido formico;
- Spettroscopia infrarossa.

Mentre per l'individuazione della percentuale di fibra PAC in miste si sono sviluppate le seguenti metodologie:

- Idrolisi del Nylon in acido cloridrico;
- Analisi densitometrica.

Nella presente relazione verranno illustrati i metodi utilizzati ed i risultati ottenuti nello sviluppo delle analisi sopraelencate al fine di individuare il sistema metodologico più adeguato per le misure richieste.

1. 2 Metodologie

2.1 Misura della percentuale di Nylon nelle fibre PAC

Nel presente capitolo verranno illustrate alcune differenti metodologie per l'individuazione della percentuale di Nylon presente nelle fibre PAC.

2.1.1 Idrolisi del Nylon

La metodologia di idrolisi del Nylon con riflusso di acido cloridrico è stata eseguita dopo prelavaggio con etere di petrolio.

PRINCIPIO

Una piccola quantità di campione viene idrolizzata a caldo a riflusso per 24 ore con acido cloridrico al 18,5 %, in questo modo si idrolizza completamente la componente Nylon della fibra, quindi sottraendo al peso iniziale la fibra rimasta dopo l'idrolisi, è possibile risalire alla composizione in % di Nylon.

PROCEDURA

- Pesare circa 1 grammo di campione in un pesafiltro di ppl
- Introdurlo in un pallone da 250 ml
- Aggiungere 100 ml di etere di petrolio
- Riscaldare il tutto a riflusso per 1 ora per estrarre l'olio di ensimaggio dalla fibra
- Recuperare la fibra lavata con etere porla in un pesafiltro introducendo il tutto in stufa a 50°C sotto vuoto per 1 ora
- Pesare circa 1 grammo di fibra lavata e asciugata porla in un pallone da 250 ml e aggiungere 100 ml di acido cloridrico al 18,5 %.
- Riscaldare il tutto a circa 70°-80° a riflusso per 24 ore
- Recuperare la fibra dopo le 24 ore di idrolisi lavandola con acqua in un complesso filtrante sotto vuoto fino a che le acque di lavaggio non risultano completamente alcaline PH 7-7.5
- Lavare infine la fibra con alcool metilico a caldo ,circa 100 ml, e porla ad asciugare per quattro ore ,comunque fino a completo asciugamento,in stufa a 100°C

- Pesare la fibra lavata ed eseguire il seguente calcolo:

  % Nylon =(P1- P2) / P1 x 100

  P1= peso fibra dopo il lavaggio con etere ed essiccamento

  P2= peso fibra dopo il lavaggio con alcol metilico ed essiccamento

2.1.2 Attacco acido del Nylon nella fibra PAC

Non si riporta per intero la procedura di tale processo di analisi vista la similitudine che essa presenta con quanto già illustrato per l'idrolisi. L'unica differenza è infatti rappresentata dall'utilizzo dell'acido formico (concentrazione 80 %) al posto dell'acido cloridrico.

2.1.3 Spettroscopia infrarossa

Tramite uno strumento Spectrum 100 Series della PerkinElmer sono state eseguite delle misure di spettroscopia infrarossa su fibre di PAC. Scopo di tale analisi è esclusivamente quello di rendere più rapida la metodologia per l'individuazione della % di PA6: le misure ad infrarosso richiedono infatti pochi minuti a differenza dei lunghi tempi richiesti dall'idrolisi con acido cloridrico.

La metodologia utilizzata prevede l'analisi della trasmittanza % del picco compreso tra 1645 e 1635 cm^{-1} e può essere sintetizzata nei seguenti passaggi:

- eseguire una misura tramite spettrometro in maniera tale che il picco a maggiore assorbimento mostri una trasmittanza di 60 ± 3 %T
- normalizzare la curva lasciando la in automatico la scelta della BaseLine
- identificare il minimo nella trasmittanza del picco compreso tra 1645 e 1635 cm^{-1}
- inserire il valore (che indicheremo con T) nell'equazione logaritmica presentata in seguito.

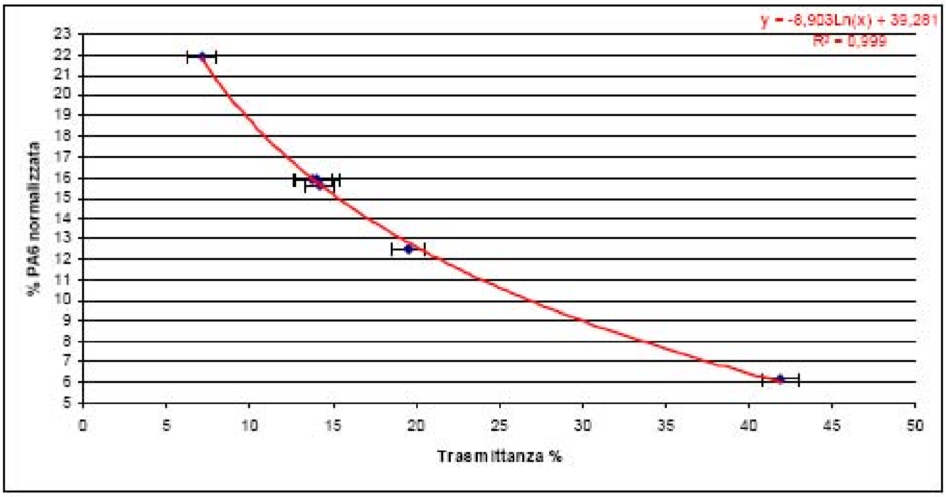
Si fa presente esclusivamente che tale ipotesi di normalizzazione del picco porta a standardizzare la curva sul picco massimo del polipropilene e quindi la calibrazione della curva è stata eseguita sulla % di PA6 normalizzata, calcolata come:

$$\textbf{\% PA6 normalizzata} = \frac{\textbf{\% PA6}}{\textbf{(\% PA6 + 100)}} * 100$$

Analogamente il valore ottenuto dall'equazione logaritmica andrà riportato alle condizioni originali e quindi il calcolo diverrà:

% PA6 normalizzata = - 8,903 * Ln (T) + 39,281

$$\% \text{ PA6} = \frac{\% \text{ PA6 normalizzata}}{(100 - \% \text{ PA6 normalizzata})} * 100$$



La metodologia può ulteriormente essere semplificata utilizzando il programma Beers Law, nel qual caso uno volta generata la curva di taratura la misura della percentuale di Nylon viene eseguita in automatico.

La metodologia utilizzata prevede l'utilizzo del programma Beer's Law 2.2.0 for Spectrum v.6 la cui retta di calibrazione è stata eseguita utilizzando dei campioni di PAC pretrattati con lavaggio a freddo in etere di petrolio ed asciugatura in forno a contenuto nominale di PA6 pari al 7, 15, 20 e 30%.

Come metodo di calcolo si è utilizzato il rapporto di intensità massima tra picchi dove:

- Picco 1 nella regione 1600-1700 cm^{-1} assegnato alla PA6
- Picco 2 nella regione 1300-1400 cm^{-1} assegnato al PP

Per le misure eseguite i campioni sono sempre stati pretrattati con lavaggio a freddo in etere di petrolio ed asciugatura in forno.

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2.2 Misura della percentuale di PAC in fibre in mista

Nel presente capitolo verranno illustrate alcune differenti metodologie per l'individuazione della percentuale di PAC presente in fibre in mista, concentrandosi in particolare sulle miste PAC-PA e PAC-PP poiché maggiormente complesse da identificare.

2.2.1 Idrolisi del Nylon

Per la procedura utilizzata nella misura della percentuale di PAC in fibre in mista tramite idrolisi si faccia riferimento a quanto presentato nel capitolo 2.1.1. Premesso che tale metodologia richiede di conoscere a priori la percentuale di Nylon presente nelle fibre PAC si può allora dire che:

% Nylon estratto =(P1- P2) / P1 x 100

P1= peso fibra dopo il lavaggio con etere ed essiccamento

P2= peso fibra dopo il lavaggio con alcol metilico ed essiccamento

e quindi per le miste PAC-PA:

$$\% \text{ PAC} = \frac{(100 - \%\text{Nylon estratto}) * \%\text{Nylon in fibra PAC}}{100 - \%\text{Nylon in fibra PAC}} + (100 - \%\text{Nylon estratto})$$

mentre per le restanti miste:

$$\% \text{ PAC} = \frac{\%\text{Nylon estratto} * 100}{\%\text{Nylon in fibra PAC}}$$

2.2.2 Densitometria

INTRODUZIONE

E' stata verificata la possibilità di identificare fibre di PAC (PP/PA6 - 80/20), PP, PET e PA6 tramite l'immersione di queste in soluzioni acquose a densità nota. Inoltre con questa procedura, è possibile stimare le composizioni percentuali di sistemi a più componenti valutando la quantità di fibra precipitata in una soluzione di densità compresa tra le densità dei due componenti.

Avendo disponibilità di uno Spettrometro IR è possibile identificare le fibre in modo più preciso ed inoltre stimare le composizioni percentuali di sistemi a più componenti.

L

IQUIDI PER L'IDENTIFICAZIONE E LA SEPARAZIONE

I liquidi utilizzati nella separazione delle fibre PET, PA6, PAC e PP sono:

- Acqua distillata e sale (Cloruro di Sodio), con una quantità di sale pari al suo limite di solubilità in acqua (358 g/l) corrispondente a circa il **26% in peso**. Si ottiene una densità della soluzione che varia con la temperatura nel seguente modo:

19°C	20°C	21°C	22°C	23°C	24°C
1,1952 g/cm^3	1,1946 g/cm^3	1,194 g/cm^3	1,1934 g/cm^3	1,1928 g/cm^3	1,1922 g/cm^3

25°C	26°C	27°C	28°C	29°C	30°C
1,192 g/cm^3	1,1911 g/cm^3	1,1905 g/cm^3	1,1899 g/cm^3	1,1893 g/cm^3	1,1888 g/cm^3

Questa soluzione permette di separare il PET (densità 1,37 g/cm^3) dal PA6 (densità 1,15 g/cm^3)

- Acqua distillata, con una densità prossima ad 1 g/cm^3, si possono separare fibre di PET e PA6 da fibre PAC e PP. La densità dell'acqua distillata varia con la temperatura nel seguente modo:

19°C	20°C	21°C	22°C	23°C	24°C
0,9984 g/cm^3	0,9982 g/cm^3	0,9980 g/cm^3	0,9978 g/cm^3	0,9975 g/cm^3	0,9973 g/cm^3

25°C	26°C	27°C	28°C	29°C	30°C
0,9970 g/cm^3	0,9968 g/cm^3	0,9965 g/cm^3	0,9962 g/cm^3	0,9959 g/cm^3	0,9956 g/cm^3

- Acqua distillata e alcol etilico 95%: la percentuale volumetrica di alcol etilico è compresa tra 48% e 51%; valore che dipende dalla temperatura dei liquidi. Si riportano in tabella le percentuali volumetriche di alcol etilico, e le rispettive temperature, che permettono di ottenere una densità della soluzione di circa **0,926 g/cm^3**.

19°C	20°C	21°C	22°C	23°C	24°C
50,9%	50,6%	50,3%	50%	49,8%	49,5%

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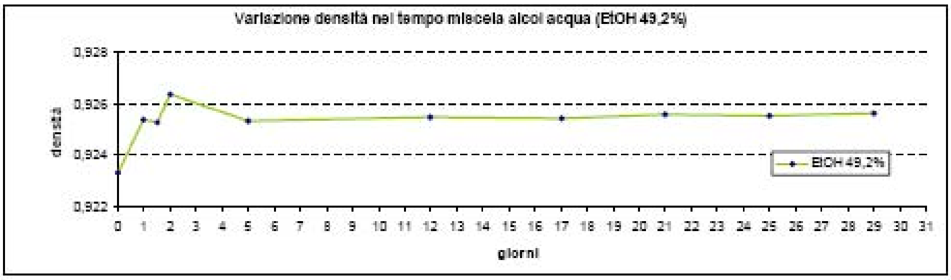
25°C	26°C	27°C	28°C	29°C	30°C
49,2%	48,9%	48,6%	48,4%	48,1%	47,8%

Questa soluzione permette di separare il PAC (densità 0,9497 g/cm^3) dal PP (densità 0,9 g/cm^3).

La variazione di densità rispetto al tempo di una soluzione acqua alcol a 25°C è rappresentata nel seguente grafico.



Come si può notare dal grafico si ha un aumento iniziale di densità dovuto ad una reazione di miscelazione leggermente esotermica che porta ad un aumento della temperatura di circa 7°C; successivamente la miscela si stabilizza ad un valore poco inferiore a 0,926 g/cm^3. Valore confermato da Perry's Chemical Engineers' Hand Book – Seventh Edition (Robert H.Perry, Don W. Green) – pagina 2-112, che da una densità di 0,92649 g/cm^3.

E' necessario quindi lasciar riposare la miscela almeno un giorno al fine di evitare che bolle di gas si attacchino alle fibre rendendo la prova inesatta. E' consigliabile inoltre miscelare nella soluzione del sapone (indicativamente 30 gocce per litro di miscela) che abbassa la tensione superficiale rendendo più facile il distacco delle bolle e non modifica la densità.

Nella tabella seguente sono stati riassunti tutti i liquidi utilizzati nei processi di separazione.

--------	PET	PA6	PAC	PP	PET + PA6	PAC + PP
PET	--------	ACQUA/SALE PET affonda PA6 galleggia	ACQUA PET affonda PAC galleggia	ACQUA PET affonda PP galleggia	--------	ACQUA PET affonda PAC+PP galleg.
PA6	ACQUA/SALE PET affonda PA6 galleggia	--------	ACQUA PA6 affonda PAC galleggia	ACQUA PA6 affonda PP galleggia	--------	ACQUA PA6 affonda PAC+PP galleg.
PAC	ACQUA PET affonda PAC galleggia	ACQUA PA6 affonda PAC galleggia	--------	ACQUA/ALCOL PAC affonda PP galleggia	ACQUA PET+PA6 affond PAC galleggia	--------
PP	ACQUA PET affonda PP galleggia	ACQUA PA6 affonda PP galleggia	ACQUA/ALCOL PAC affonda PP galleggia	--------	ACQUA PET+PA6 affond PP galleggia	--------
PET + PA6	--------	--------	ACQUA PET+PA6 affond PAC galleggia	ACQUA PET+PA6 affond PP galleggia	--------	ACQUA PET+PA6 affond PAC+PP galleg
PAC + PP	ACQUA PET affonda PAC+PP galleg	ACQUA PA6 affonda PAC+PP galleg.	--------	--------	ACQUA PET+PA6 affond PAC+PP galleg	--------

PROCEDURA DI IDENTIFICAZIONE

1. Materiale necessario: acqua distillata, alcol 95%, sale (Cloruro di Sodio), recipiente in vetro.
2. Taglio del fascio di fibre: il fascio di fibre deve essere tagliato tra due punti di interlacciatura in modo che le singole fibre risultino divise e con una lunghezza di 5 millimetri; questo per evitare che bolle di aria rimangano intrappolate nei fasci interi di fibre sfalsando la misura.
3. Immersione delle fibre nelle soluzioni: immergere le fibre tagliate in un recipiente riempito con acqua distillata: se affondano sono costituite da PET o PA6 e per la definitiva identificazione, si deve procedere con l'immersione in acqua e sale. Se le fibre invece galleggiano sono costituite da PAC o PP e per la definitiva identificazione, si deve procedere con l'immersione in acqua e alcol.

PROCEDURA DI SEPARAZIONE

1. Materiale necessario: acqua distillata, alcol 95%, sale (Cloruro di Sodio), recipiente in vetro, sistema di aspirazione (siringa), filtro.
2. Taglio del fascio di fibre: il fascio di fibre deve essere tagliato in modo che le singole fibre risultino ben divise le une dalle altre e con una lunghezza di 5 millimetri. Il taglio va quindi

eseguito tra due punti di interlacciatura (figura 1) e le fibre, se non completamente separate, devono essere divise manualmente (figura 2). Indicativamente sono sufficienti 30 mg per i sistemi binari e 50 mg per i sistemi a più di due componenti.

3. Immersione delle fibre nella soluzione: immergere le fibre nella soluzione appropriate, seguendo le indicazioni date nella tabella riassuntiva, ed agitare bene in modo da distribuire le fibre nel liquido. Il tempo per la separazione dipende dal tipo di soluzione utilizzata:
   - 2^h30^m / 3^h ore per la soluzione acqua e alcol;
   - 30^m per le altre soluzioni (acqua ed acqua/sale).

   Prestare attenzione che tutte le fibre si siano separate, in quanto capita che alcune fibre (di diverso materiale) si annodino tra di loro, figura 3, e rimangano in sospensione; in tal caso aiutare la separazione tramite l'utilizzo di pinze di lunghezza adeguata.
4. Aspirazione: aspirare le fibre in superficie con una siringa o con altri strumenti adatti.
5. Filtraggio: filtrare il contenuto della siringa e lasciare asciugare le fibre in modo da poter eseguire la misura del peso; si può accelerare l'asciugatura utilizzando un forno. In tal caso portare la temperatura a 75°C e se l'apparecchiatura lo permette, creare il vuoto all'interno del forno. Nel caso in cui si utilizzi acqua e sale è necessario lavare le fibre con acqua distillata, una volta estratte dalla miscela; questo perchè il sale si deposita sulla fibra e modifica il peso della stessa.

SPETTROMETRO IR

Con un Spettrometro IR è possibile identificare una fibra in modo molto preciso tramite un'analisi ed una comparazione con i dati in letteratura. Per il calcolo delle percentuali di un sistema a più componenti, il metodo consta in una separazione manuale dei diversi fasci di fibra, in una analisi degli stessi al fine di verificarne la natura e la corretta separazione ed infine, in una misura del peso dei singoli fasci attraverso una bilancia analogica. E' così possibile calcolare le percentuali ponderali e volumetriche dei vari componenti.

3 Risultati ottenuti

3.1 Misura della percentuale di Nylon nelle fibre PAC

3.1.1 Idrolisi del Nylon

Nei capitoli a seguire verranno presentati i risultati di misura della percentuale di Nylon nelle fibre PAC tramite idrolisi in acido cloridrico. Si è dapprima verificata la capacità di estrarre tutto il Nylon in fibre contenenti diverse percentuali dello stesso e successivamente si è analizzato il tempo minimo richiesto per tale analisi.

3.1.1.1 Idrolisi del Nylon in fibra PAC a diverse composizioni

Vengono di seguito presentati i risultati inerenti all'idrolisi del Nylon in fibre PAC a differenti concentrazioni nominali di PA con fibre prelevate da tappeto. Per tali misure si è utilizzato un tempo di estrazione di 24 ore.

% di PA6 misurata dopo idrolisi con acido cloridrico al 18,5%			
Campione	% PA6 nominale	TiO_2	% PA6 (24 ore)
7% PAC DU	7	si	6,6
15% PAC DU	15	si	14,3
20% PAC BT	20	no	18,9
20% PAC DU	20	si	18,9
20% PAC 2DU	20	doppio	18,5
30% PAC DU	30	si	28,1

Al termine di tutte le prove di idrolisi è stata eseguita una misura di spettroscopia infrarossa, la quale ha verificato che non erano più presenti tracce di polipropilene nel residuo. Per tale ragione si ritiene che la percentuale di Nylon misurata, possa essere ritenuta la percentuale reale di PA6 contenuta nelle fibre di Matrix.

3.1.1.2 Idrolisi del Nylon in fibra PAC a differenti tempi di analisi

Verificata la buona capacità dell'acido cloridrico di idrolizzare il Nylon presente in fibre PAC si sono eseguite differenti prove al fine di valutare il tempo minimo necessario di estrazione per una corretta misura. Per tale analisi si è utilizzata della fibra PAC a concentrazione nominale del 20 % (concentrazione reale stimata attraverso l'analisi dei parametri di processo pari al 20,2 %).

Idrolisi in HCL al 17,5 %			
tempo [ore]	**PAC**		**PAC**
	p iniz.	**p idrol.**	**% Nylon**
2	1.0453	0.8479	**18.9**
	1.0818	0.8750	**19.1**
MEDIA	1.0636	0.8615	**19.0**
4	1.0881	0.8755	**19.5**
	1.0804	0.8696	**19.5**
MEDIA	1.0843	0.8726	**19.5**
6	1.1481	0.9298	**19.0**
	1.0156	0.8189	**19.4**
	1.1003	0.8845	**19.6**
	1.0881	0.8790	**19.2**
	1.0249	0.8289	**19.1**
	1.0791	0.8663	**19.7**
	1.0745	0.8686	**19.2**
MEDIA	1.0758	0.8680	**19.3**
8	1.0218	0.8230	**19.5**
	1.0275	0.8270	**19.5**
MEDIA	1.0247	0.8250	**19.5**
16	1.0317	0.8203	**20.5**
	1.0040	0.8047	**19.9**
MEDIA	1.0179	0.8125	**20.2**
24	1.0145	0.8094	**20.2**
	1.0265	0.8188	**20.2**
MEDIA	1.0205	0.8141	**20.2**

3.1.2 Attacco acido del Nylon nella fibra PAC

Per le analisi di trattamento delle fibre di PAC con acido formico e solforico si è utilizzata una bava contenete una percentuale nominale di Nylon del 20%. Nelle seguenti tabelle vengono presentati i risultati di perdita in peso ottenuta dopo lavaggio in etere e dopo il successivo attacco con acido formico 80%. I risultati mostrano che l'etere di petrolio rimuove l'olio di ensimaggio in modo completo (teorico 1,4%), mentre la perdita in peso successiva è stimabile in circa 0,56% con una deviazione standard di 0,06% .

Perdita di peso dopo lavaggio in Etere di Petrolio			
campione	**peso iniziale**	**peso finale**	**% di estratto in etere**
1	1,2428	1,2246	1,46
2	1,1224	1,1058	1,48
3	1,1590	1,1419	1,48
4	1,2223	1,2047	1,44
5	1,2575	1,2396	1,42
6	1,1661	1,1491	1,46
7	1,1929	1,1759	1,43
8	1,2234	1,2046	1,54
9	1,1739	1,1554	1,58
10	1,1553	1,1380	1,50
media			**1,48**
dev.st			**0,05**

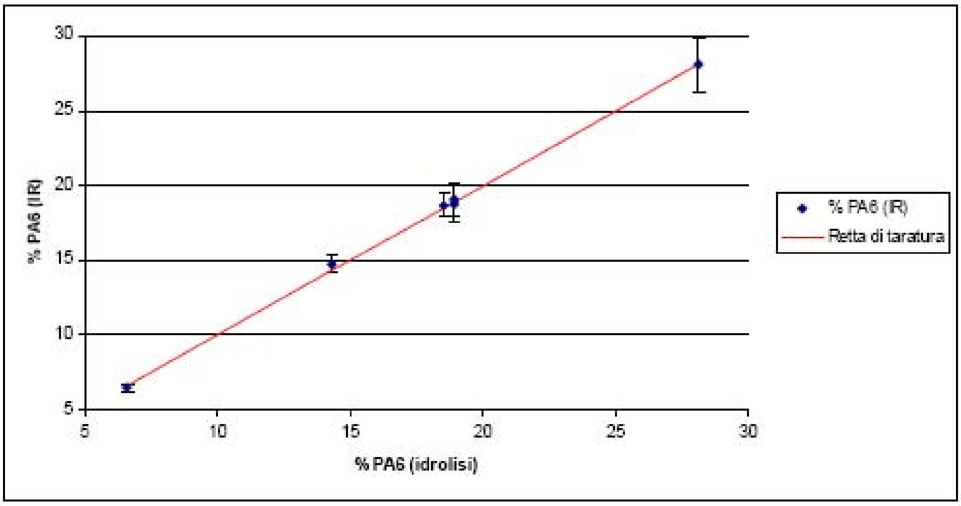
Perdita di peso dopo trattamento con acido formico all'80%			
campione	**peso iniziale**	**peso finale**	**% Nylon solubile**
1	1,2246	1,2171	0,61
2	1,1058	1,0989	0,62
3	1,1419	1,1356	0,55
4	1,2047	1,1976	0,59
5	1,2396	1,2320	0,61
6	1,1491	1,1423	0,59
7	1,1759	1,1707	0,44
8	1,2046	1,1986	0,50
9	1,1554	1,1494	0,52
10	1,1380	1,1322	0,51
media			**0,56**
dev.st			**0,06**

3.1.3 Spettroscopia infrarossa

Vengono di seguito presentati i risultati inerenti all'analisi del Nylon in fibre PAC a differenti concentrazioni nominali di PA con fibre prelevate da tappeto tramite spettroscopia infrarossa. I risultati ottenuti mostrano come sei misure di spettroscopia possano essere sufficienti per valutare la percentuale di poliammide media contenuta nelle fibre di PAC con ottima approssimazione. Poiché l'analisi è puntuale e la concentrazione di Nylon non è uniforme nella fibra la deviazione standard risulta piuttosto elevata.

Per tale analisi si sono utilizzate le medesime fibre provenienti da tappeto utilizzate per l'analisi: idrolisi del Nylon in fibra PAC a diverse composizioni.

% di PA6 misurata tramite spettroscopia infrarossa						
	7% PAC DU	**15% PAC DU**	**20% PAC BT**	**20% PAC DU**	**20% PAC 2DU**	**30% PAC DU**
% PA6 idrolisi	**6,6**	**14,3**	**18,9**	**18,9**	**18,5**	**28,1**
	6,1	13,9	17,8	18,0	18,9	29,6
	6,5	15,2	19,0	19,2	19,9	28,8
	6,8	14,5	19,9	17,5	18,4	27,4
	6,6	14,7	18,5	19,5	19,2	27,2
	6,4	14,6	18,6	20,8	18,1	25,5
	6,3	15,6	20,9	18,0	17,8	30,5
media	**6,5**	**14,8**	**19,1**	**18,8**	**18,7**	**28,0**
dev.st	**0,3**	**0,6**	**1,1**	**1,2**	**0,8**	**1,8**



I risultati ottenuti su filo di PAC a contenuto nominale di PA del 20% prelevato da una bobina in mista di PAC – PP sono i seguenti attraverso la metodica che prevede l'utilizzo del software Beers Law sono i seguenti:

FTIR – PAC a 20% di contenuto nominale								
Campione	1	2	3	4	5	6	**media**	**DS**
% PA6	20,5	19,6	20,6	19,7	20,1	19,6	**20,0**	**0,5**

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3.2 Misura della percentuale di PAC in fibre in mista

3.2.1 Idrolisi del Nylon

Nei capitoli a seguire verranno presentati i risultati relativi all'idrolisi del Nylon in fibre in mista PAC-PP e PAC-PA6 a differenti tempi di analisi.

Per il calcolo della percentuale di PAC presente nella mista si è utilizzata la % di Nylon estratta dalla fibra PAC nel medesimo tempo di idrolisi.

LA verifica della bontà della misura è stata eseguita misurando il titolo della fibra PAC e delle fibre in mista e calcolando quindi il rapporto percentuale tra le fibre componenti la mista:

$$\%\ PAC = \frac{\text{Titolo PAC} * 100}{\text{Titolo mista}}$$

Si è infine stimata la percentuale teorica di Nylon estraibile dalla mista assumendo che la fibraPAC contenesse una % di Nylon pari al 20,2%.

3.2.1.1 Idrolisi del Nylon in miste PAC/PP

I risultati ottenuti a differenti tempi di analisi per l'idrolisi del Nylon in miste PAC/PP vengono presentati nella seguente tabella:

Idrolisi in HCL al 17,5 %						
	PAC + PP		PAC	PAC + PP		
tempo [ore]	p iniz.	p idrol.	% Nylon	% Nylon	% PAC	% PP
2	1.0764	0.9580	19.0	11.0	57.9	42.1
4	1.0568	0.9384	19.5	11.2	57.4	42.6
6	1.1325	1.0045	19.3	11.3	58.5	41.5
8	1.0239	0.9072	19.5	11.4	58.5	41.5
16	1.1153	0.9915	20.2	11.1	55.0	45.0
24	1.0985	0.9755	20.2	11.2	55.4	44.6
Misura dei titoli						
	PAC	PAC + PP	PAC	PAC + PP		
	dTex		% Nylon	% Nylon	% PAC	% PP
	1181	2154				
	1215	2149				
	1180	2113				
MEDIA	1192	2139	20.2	11.3	55.7	44.3

Come si può osservare per fibre in mista PAC/PP 6 ore di idrolisi sono sufficienti ad ottenere un valore della % di Nylon confrontabile con il valore teorico.

3.2.1.2 Idrolisi del Nylon in miste PAC/PA6

I risultati ottenuti a differenti tempi di analisi per l'idrolisi del Nylon in miste PAC/PA6 vengono presentati nella seguente tabella:

Idrolisi in HCL al 17,5 %						
	PAC + PA6		PAC	PAC + PA6		
tempo [ore]	p iniz.	p idrol.	% Nylon	% Nylon	% PAC	% PA6
2	1.1067	0.4839	19.0	56.3	54.0	46.0
4	1.0234	0.4459	19.5	56.4	54.1	45.9
6	1.0463	0.4538	19.3	56.6	53.8	46.2
8	1.0032	0.4348	19.5	56.7	53.8	46.2
16	1.1398	0.4958	20.2	56.5	54.5	45.5
24	1.0247	0.4439	20.2	56.7	54.3	45.7
Misura dei titoli						
	PAC	PAC + PA6	PAC	PAC + PA6		
	dTex		% Nylon	% Nylon	% PAC	% PA6
	1181	2222				
	1215	2212				
	1180	2204				
MEDIA	1192	2213	20.2	57.0	53.9	46.1

Analogamente a quanto osservato per miste PAC/PP anche per fibre in mista PAC/PA6 6 ore di idrolisi sono sufficienti ad ottenere un valore della % di Nylon confrontabile con il valore teorico.

3.2.2 Densitometria

E' stata verificata la possibilità di identificare fibre di PAC (PP/PA6 - 80/20), PP, PET e PA6 tramite l'immersione di queste in soluzioni acquose a densità nota. Inoltre con questa procedura, è possibile stimare le composizioni percentuali di sistemi a più componenti valutando la quantità di fibra precipitata in una soluzione di densità compresa tra le densità dei due componenti.
Avendo disponibilità di uno Spettrometro IR è possibile identificare le fibre in modo più preciso ed inoltre stimare le composizioni percentuali di sistemi a più componenti.

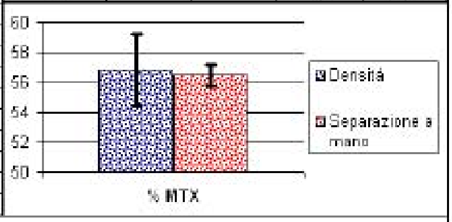
3.2.2.1 Ripetibilità statistica per miste PAC-PP

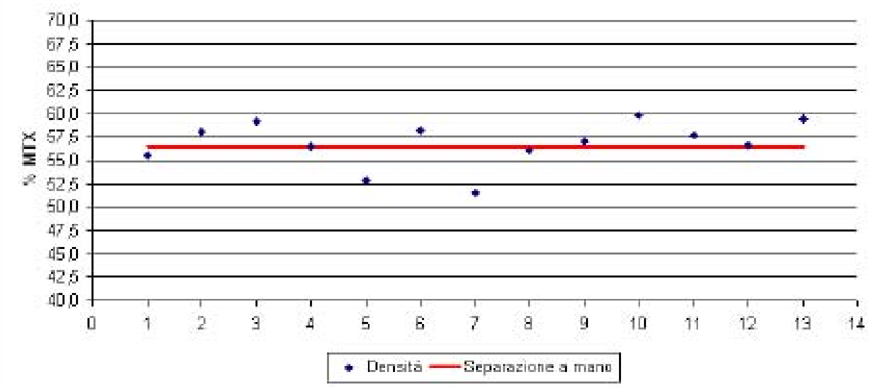
L'attività condotta è mirata alla valutazione dell'affidabilità della metodica di separazione tramite densimetria sulle miste PP/PAC, che risulta essere, a causa della ridotta differenza di densità, la più difficile da analizzare.

I risultati ottenuti e la relativa analisi statistica vengono riportati in figura. I risultati indicano una buona corrispondenza tra i dati ottenuti tramite separazione manuale e la misura ottenuta per separazione densitometrica.

Densità				
Senza lavaggio olio				
CAMPIONE	Peso tot	Peso PP	% PP	% MTX
	[mg]	[mg]	[%]	[%]
1	34,0	15,1	44,4	55,6
2	31,0	13,0	41,9	58,1
3	33,0	13,5	40,9	59,1
4	32,9	14,3	43,5	56,5
5	34,2	16,1	47,1	52,9
6	32,8	13,7	41,8	58,2
7	29,5	14,3	48,5	51,5
8	31,4	13,8	43,9	56,1
9	30,0	12,9	43,0	57,0
10	31,6	12,7	40,2	59,8
11	31,9	13,5	42,3	57,7
12	31,1	13,5	43,4	56,6
13	40,6	16,5	40,6	59,4
MEDIA			**43,2**	**56,8**
DS			**2,4**	**2,4**

Separazione a mano				
Senza lavaggio olio				
CAMPIONE	Peso tot	Peso PP	% PP	% MTX
	[g]	[g]	[%]	[%]
1	0,4875	0,2107	43,2	56,8
2	0,4637	0,1995	43,0	57,0
3	0,446	0,1978	44,3	55,7
MEDIA			**43,5**	**56,5**
DS			**0,7**	**0,7**





Dati misurati e loro analisi statistica

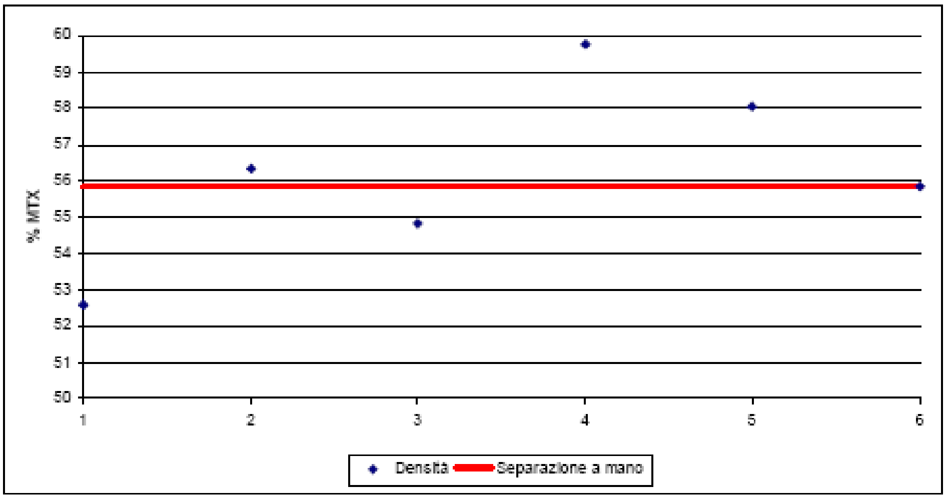
3.2.2.2 Ripetibilità statistica per miste PAC-PP con quantità elevate di fibra in soluzione

Le prove, rispetto a quanto fatto in precedenza, sono state condotte utilizzando un litro di soluzione ed aumentando progressivamente il quantitativo di fibra introdotta.

Prove con l'utilizzo di 0.1 g di fibra: i risultati ottenuti in una prima sessione di prova vengono riportati nella pagina seguente. Come si può osservare i risultati sono confrontabili con quelli ottenuti con 30 mg di fibra introdotta sia come valore medio che come deviazione standard.

Si fa presente che una seconda sessione di misure non ha prodotto alcun risultato, l'elevato quantitativo di soluzione e la relativa necessità di aumentare le dimensioni del contenitore comportano un minore controllo nell'evaporazione dell'alcool durante i tre giorni di stazionamento. Sebbene le condizioni ambientali fossero immutate così come la tipologia di soluzione rispetto alla prima prova, una verifica della densità ha mostrato come la soluzione fosse eccessivamente densa per riuscire a separare le fibre che hanno raggiunto il galleggiamento in maniera quasi totalitaria.

Prima sessione di prove con quantitativo superiore a 100 mg						
Campione		**PP**	**PAC**	**PP + PAC**	**% PP**	**% PAC**
	[mg]	[mg]	[mg]	[mg]	[%]	[%]
1	116,8	55,4	61,6	116,9	47,4	52,6
2	114,8	50,1	64,6	114,7	43,7	56,3
3	116,0	52,4	63,6	116,1	45,2	54,8
4	113,8	45,8	67,9	113,7	40,3	59,7
5	114,3	48,0	66,4	114,3	42,0	58,0
6	115,3	51,0	64,5	115,4	44,2	55,8
MEDIA					43,8	56,2
DS					**2,5**	**2,5**



Dati misurati e loro analisi statistica

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Prove con l'utilizzo di 0.5 g di fibra: anche in questo caso sono state eseguite due differenti sessioni di prova. In entrambi i casi si è misurata la densità della soluzione e verificato che rientrasse nei parametri richiesti.

Nella prima sessione le fibre sono state tagliate con lunghezza approssimativa di 5 mm e l'interazione tra le fibre ha fatto si che le bave di PP trasportassero con loro anche quelle di PAC rendendo la misura decisamente poco significativa.

Per ovviare a tale problema si è deciso di ridurre la dimensione delle fibre in una seconda sessione a 1 – 2 mm, tuttavia ciò non ha comportato alcun miglioramento.

4 Conclusioni

Alla luce dei risultati presentati è possibile trarre le seguenti conclusioni:

Misura della percentuale di Nylon nelle fibre PAC

Idrolisi del Nylon

L'idrolisi del Nylon a diverse composizioni ha mostrato come 24 ore di analisi consentano di misurare la percentuale di PA6 presente nella fibra PAC con ottima precisione. In seguito lo studio di un filo a percentuale nominale del 20% a differenti tempi di idrolisi ha evidenziato come l'analisi su sei ore presenti una discreta stabilità della misura e sebbene essa tenda ad essere leggermente sottostimante consente di individuare con certezza il contenuto nominale di Nylon presente in fibra.

Attacco acido del Nylon nella fibra PAC

L'utilizzo di acido formico all'80% consente di sviluppare una metodologia che non è in grado di fornire una misura quantitativa tuttavia essa garantisce un riconoscimento immediato della fibra PAC rispetto alle fibre in Nylon le quali subiscono una perdita di peso decisamente superiore o rispetto a fibre di PP le quali non subiscono alcuna perdita di peso.

Spettroscopia infrarossa

L'utilizzo di uno spettroscopio ad infrarosso consente il riconoscimento immediato delle fibre di PAC senza bisogno di alcun pretrattamento ed è sufficiente avere a disposizione una singola bava. Per ottenere dei valori quantitativi significativi sono necessarie differenti misure poiché l'analisi è puntuale e le bave presentano un'elevata variabilità nella percentuale di PA6 presente a livello microscopico; variabilità dovuta al processo produttivo stesso. Ciò nonostante il metodo risulta decisamente il più rapido e sufficientemente preciso in particolar modo se le fibre vengono precedentemente lavate in etere di petrolio al fine di rimuovere l'olio di ensimaggio. Il metodo presenta come unico difetto la necessità di disporre a priori di campioni a percentuale di PA6 nota al fine di generare una curva di taratura specifica per lo strumento utilizzato.

Misura della percentuale di PAC in fibre in mista

Idrolisi del Nylon

I risultati ottenuti per miste PAC-PP e PAC-PA6 evidenziano come tale metodologia sia molto precisa per misure quantitative, essa richiede tuttavia di conoscere a priori la percentuale di Nylon presente nella fibra PAC. Nello specifico l'analisi dei tempi ha evidenziato come 6 ore di idrolisi siano sufficienti ad ottenere dei valori con una precisione sufficiente.

Sebbene il metodo sia stato applicato esclusivamente alle miste PAC-PP e PAC-PA6 essa è applicabile anche a miste PAC con poliestere il quale non subisce perdite di peso significative in acido cloridrico al 17,5%.

Densitometria

Le prove condotte si sono concentrate su miste PAC-PP essendo il caso con la minore differenza di densità e quindi il più complesso. Tali misure hanno evidenziato che la metodologia migliore è quella con quantità di fibra ridotte (30 mg) la quale porta ad una buona corrispondenza tra i dati ottenuti tramite separazione manuale e la misura ottenuta per separazione densitometrica.
Oltre alla buona precisione la metodologia offre il vantaggio di essere applicabile a qualunque mista; di contro tuttavia si riescono ad analizzare solo piccole quantità, è estremamente laboriosa e necessità di tempi lunghi e ottima manualità e accuratezza dell'operatore. Tale metodo diventa indispensabile in presenza di miste triple (es: PAC-PP-PET) poiché consente di ricondursi a sistemi binari e poter quindi procedere con la metodologia di idrolisi o eseguire una nuova misura densitometrica.

Metodologie combinate per la misura della percentuale di PAC in fibre in mista

In conclusione in presenza di miste di tipo ternario è sicuramente necessario l'utilizzo della metodologia densitometrica al fine di ricondursi a sistemi misti PAC-PP o PAC-PA6. Per l'analisi di tali miste può essere utilizzata nuovamente l'analisi densitometrica oppure si può utilizzare la metodologia ad idrolisi la quale garantisce una maggiore precisione nel risultati e tempi inferiori visto che 6 ore di idrolisi sono sufficienti per ottenere buone misure quantitative. Tale metodologia di analisi necessita tuttavia di conoscere la percentuale di Nylon presente nella fibra PAC. Sebbene l'idrolisi della sola fibra PAC conduca a buoni risultati essa appare molto difficile in presenza di fibre in mista poiché sarebbe necessario disporre di quantitativi notevoli di fibra e difficilmente ricavabili tramite analisi densitometrica. Con tali premesse si può dedurre come l'analisi di spettroscopia infrarossa sia la maggiormente adeguata a tale scopo poiché consente di distinguere in maniera immediata le fibre PAC dalle restanti, necessita di piccoli quantitativi e sebbene siano necessarie almeno 6 misure differenti è molto rapida.

Il sistema metodologico che pare quindi maggiormente idoneo è il seguente:

Miste ternarie		**Miste PAC/PP; PAC/PA6**		**Nylon presente in fibra PAC**
Analisi densitometrica	=>	Idrolisi in 6 ore	=>	Spettroscopia infrarossa

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IDENTIFICATION METHODOLOGIES FOR PROPYLAMIDECOMPOSITE FIBER.

INTRODUCTION

Following the research developed by Aquafil spa (Arco, Trento-Italy) on the production of a new composite-like fiber, in the Laboratory of Polymers and Composite of the University of Trento various methodologies have been optimised and used for the characterization of the products.

Propylamidecomposite fibers are produced by a Reactive Spinning of polymeric blends based on polypropylene (PP) and polyamide (PA). Significant mechanical properties improvements can be achieved as reported (1).

Reactive Blending of PA and PP will allow and induce the creation of a see-in-the-island type structure, whereas polyamide islands, are formed and are sheeted by the inert polyolefin see. Scientific evidences do exist that, as PA content increases, the size of islands will increase up to a point, where 'bridges' will start connect islands and create a more complex microstructure. Experimental evidences (2) suggests that an extruded 50 wt % PP / 50 wt% PA, can still maintain this island-in-the-see microstructure. Also (3) provide experimental evidences that an extruded 50wt% PP/50wt% PA blend is characterized by a dispersed microstructure of PA inside a PP matrix.

In the case of Reactive Spinning, PA is shaped in form of fibrils elongated in the direction of the fiber axis and surrounded by the polyolefin polymer. However, due to the novelty of the new fiber, it is more difficult to have scientific information about the upper limit of the Polyamide content in the Propylamidecomposite fiber. Therefore, we prudently suggest to consider a maximum limit of PA of 45wt%.

1) Fiber Composition determination: the main procedures used by the present Laboratory are:
- Differential Scanning Calorimetry (DSC)
- Infrared Spectroscopy in ATR configuration (FTIR-ATR)
- Density Measurement

Also XR analysis is interesting, but it requires a more specific equipment, not always available in common analytical labs.

2) Fiber Microstructure determination: the main procedure used by the present Laboratory is:
- Scanning Electronic Microscope (SEM)

Methodologies Description.

DSC.

1. About 15-20 mg of continuous filament are loaded in an aluminium DSC pan. It is recommended to use a large pan of about 160 microliter.
2. Thermal scan is performed between 0°C and 260°C by using a heating rate of 10°C/min flushing nitrogen at 100ml/min. A single heating scan will provide a standard information on the fiber characteristics, whereas more details can be achieved by using a cycle of heating-cooling-heating:
   a) During the first heating scan, the melting peak of both the PP and PA phase are registered at about 170 and 220°C respectively.
   b) The second heating scan evidences the melting peak of PP at about 165°C, whereas the melting peak of PA is located at about 220°C. The integration of these two peaks is more representative of the real composition, because the processing effects and the orientation phenomena have been delayed after the first scan. The melting enthalpy is related to the percentage of crystalline phase of the two components, that could approximately evaluated by referring to the melting enthalpy of the pure components $E_{PP\text{-}100\%}$ and $E_{PA\text{-}100\%}$ according to the equations (1) and (2) where $E_{P\text{-}MTX}$ and $E_{PA\text{-}MTX}$ are the melting enthalpy of the two polymer in the MTX filament.
   $$P_{PP}\ \% = 100 \times E_{P\text{-}MTX} / E_{PP\text{-}100\%} \quad (1)$$
   $$P_{PA}\ \% = 100 \times E_{PA\text{-}MTX} / E_{PA\text{-}100\%} \quad (2)$$
   c) Further information can be obtained during a controlled cooling stage in same interval of 260-0°C with a cooling rate of –10°C/min. The crystallization peak of polypropylene is always detectable at about 120°C. The crystallization peak of PA is typically a large peak between 190 and 160°C. In the case of the Propylamidecomposite Fiber family it is strongly reduced and tends to disappears in dependence of the chemical reaction between the two polymers during reactive blending. This phenomena is called 'co-crystallisation', as reported by the literature, and differentiate this fiber family from the commonly used physical fiber blends (fiber mixtures).

FTIR.

The FTIR (infrared spectroscopy in solid phase) is a complementary technique. The BCF product is directly tested in the range 4000-650 cm^{-1}(sensitivity 4 cm^{-1}). The typical PA peaks are located at about 3300, 3080, (2930 and 2860), 1640 and 1535 cm^{-1}, whereas PP shows peaks at about 2950, 2920, (2870 and 2940), 1455 and 1375 cm^{-1}. The presence of the main peak will qualitatively identified the MTX filament. In the range 3000-2800 cm^{-1}, the peaks are partially overlapped.

A quantitative analysis can be obtained by comparing the intensity of the peak at 1640cm^{-1} or 3300cm^{-1} ($I_{PA\text{-}MTX}$) and 1455cm^{-1} ($I_{P\text{-}MTX}$) in MTX filament and in the pure PP or PA filament according to the equations 3 and 4:

$$P_{PP}\ \% = 100 \times I_{P\text{-}MTX} / I_{PP\text{-}100\%} \quad (3)$$
$$P_{PA}\ \% = 100 \times I_{PA\text{-}MTX} / I_{PA\text{-}100\%} \quad (4)$$

For a good quantitative analysis, the operator should take care to use the same amount of fiber and to apply the same contact pressure on the crystal. A more sophisticated evaluation will consider an internal standard in order to normalize the relative intensities of the three spectra (PP, PA and MTX), for instance the peaks at about 2950-2920 cm^{-1}.

DENSITY

Blend density can be measured by the Archimedean methodology following the norm ASTM D792. For the specific case the Propylamidecomposite yarn, sample is prepared as follows:

1. is gently scoured in warm water to remove sin finish;
2. is dried at 100°C for at least 15 min and than cooled to room temperature;
3. yarns weight is measured in air w_{air};
4. yarns weight is measured in ethyl alcohol having a purity of 95%, w_{Et}; ethanol temperature is also measured to compensate its density ρ_{Et} as a function of temperature;
5. Density ρ is calculated according to ASTM D792 norms with equation (5):

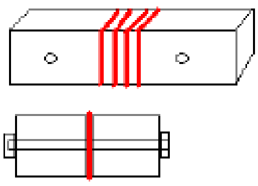
$$\rho_{Et} = \rho_{Et}\, w_{air} / (w_{air} - w_{Et}) \qquad (5)$$

The experimental error is ± 0.001.

SEM

Analysis of the microstructure, i.e. of the presence, size and distribution of the PA microfibrils embedded inside the polyolefin matrix, is carried out on yarns cross-section after a proper sample preparation.

1. The yarn is wrapped around a metal square-shaped metal sample-holder typically made in AISI 304 steel, as in (1) of sample-holder sketch (where red lines indicates the wrapped yarn), with typical dimensions of 45x10x5 mm. Sample-holder edges must be as sharp as possible. A second bar having the same size is joined to the first, using two screws, as in (2) of sample-holder sketch.



1. Wrapping of the yarn around the metal bar

2. Side view after positioning of the second square bar and yarn cut

2. The sample-holder with the wrapped yarn and a sharp razor blades are placed inside a liquid nitrogen bath for at least 5 minutes.
3. Immediately after removal from the liquid nitrogen bath, the yarn is carefully cut using the razor blade at the edges were the two bars are joining. Cutting is done by a rapid sliding of the razor blade on the sample-holder surface. An appropriate pressure must be exerted on the sample-holder surface while sliding and an appropriate cut speed must be used in order

to have a proper plain cut surface of the yarn. After cutting, only the yarn clipped inside the two metal bars remains, as in (2) (red line) of sample-holder sketch. A visual inspection using an Optical Microscope with a minimum magnification of 50x allows to verify the quality of the cut surface. Eventually, when this is not properly done, the procedure must be repeated.

4. The sample-holder is then placed inside a formic acid bath at room temperature for at least 60 minutes, in order to remove the nylon fibrils by chemical dissolution.
5. The sample is than coated by a conductive layer using the standard metallographic SEM procedure, such as through a silver metallization in a vacuum chamber.
6. A morphological SEM analysis is that carried out in order to evidence the location of the nylon fibrils inside fiber cross-section, now visible in form of holes.
7. When necessary, e.g. to verify the existence of hole previously present (e.g. hollow fibers) the surface analysis can also be repeated without the chemical attach in the formic acid bath.

EXPERIMENTAL APPLICATION OF TESTING METHODOLOGIES

Three different industrial BCF Propylamidecomposite yarns were produced by Aquafil having a composition range from 15wt% to 25wt% of PA6.
DSC, FITR-ATR, density and SEM analysis were preformed on the three types of yarns.

- Results of DSC analysis are reported in Fig.1 to 4. Fig.1 present the first Heating Cycle, Fig.2 the Cooling Cycle, showing the co-crystallisation, Fig.3 the second heating Cycle. Fig.4 plots the relationships between the nominal PA6 wt% content and the Melting Heat or the Melting Enthalpy.
- Results of FITR are reported in Fig.5.
- A comparison between nominal composition, DSC and FITR results is reported in Fig.6.
- The correlation between the nominal composition and density is reported in Fig.7; a slight deviation from the linear relationship is evidenced.
- SEM metallographic analysis are reported in Fig.8 (15wt% PA6), 9 (20wt%PA6) and 10 (25wt%PA6).

LIST OF FIGURES

References.

(1) I.Grof, M.Sain, O.Drcova, Structure-Properties Relationship of Modified Polypropilene-Polycaprolactamide Fiber, J.of Applied Polymer Science, vol.44 1061-1068 (1992).

(2) J.E. Bidaux, G.D.Smith, J.E.manson, C.Plummer, J.Hilborn, Fusion Bonding of maleic anhydride grafted Polypropilene-Polyamide 6 blends to polyamide 6, Polymer, Vol.39, n.24, pp.5939-5948, 1998.

(3) G.Pompe, P.Ploetschke, J.Pionteck, Reactive Melt Blending of Modified Polyamide and Polypropilene: Assessment of Compatibilisation by Fractionated Crystallisation and Blemd Morphology, Journal of Applied Polymer Science, Vol.86, pp.3445-3453, 2002.

(4) J. Teng1, J.U. Otaigbe, E. P. Taylor, Reactive Blending of Functionalized Polypropylene and Polyamide 6: In situ Polymerization and In situ Compatibilization, Polymer Engineering And Science, , Vol. 44, No. 4, pp.648-659, April 2004.

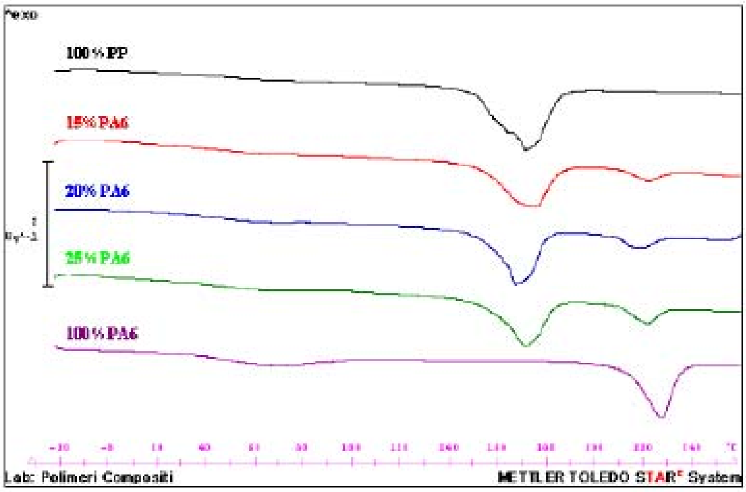


Grafico 5-3: Propylamidecomposite Fibre, I SCAN (riscaldamento -30°C ? 260°C)

Fig.1 – DSC analysis of Propylamidecomposite fibers – I[st] Heating Cycle.

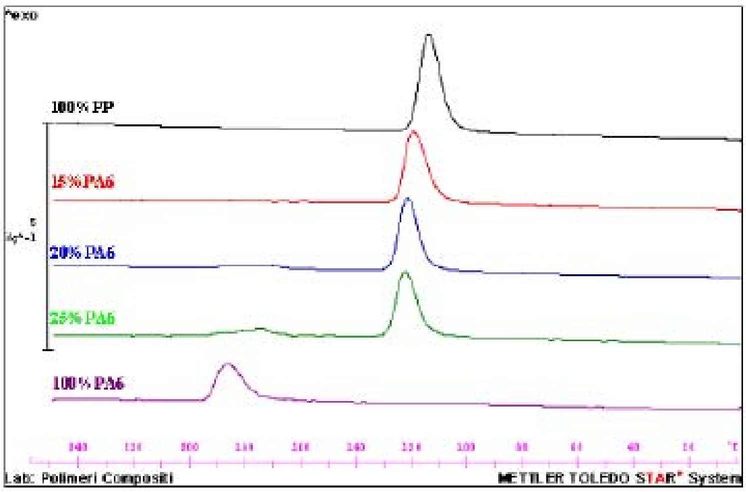


Grafico 5-4: Propylamidecomposite Fibre, II SCAN (raffreddamento 260°C ? 0°C)

Fig.2 – DSC analysis of Propylamidecomposite fibers – Cooling Cycle

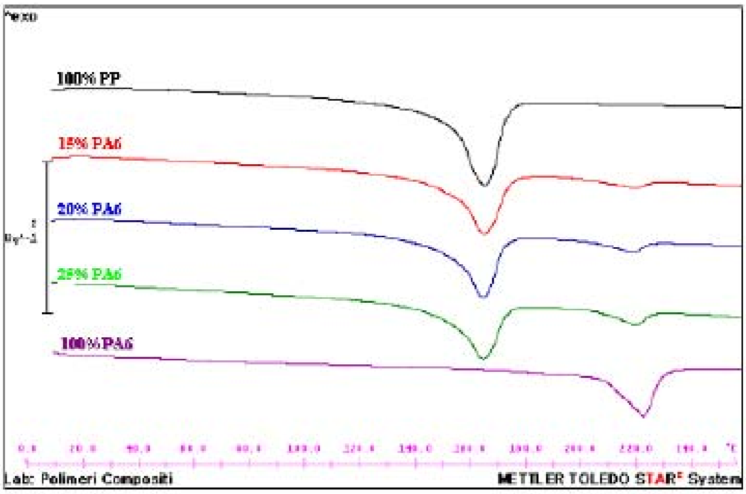


Grafico 5-5: Propylamidecomposite Fibre, III SCAN (riscaldamento 0°C ? 360°C)

Fig.3 – DSC analysis of Propylamidecomposite fibers – IInd Heating Cycle

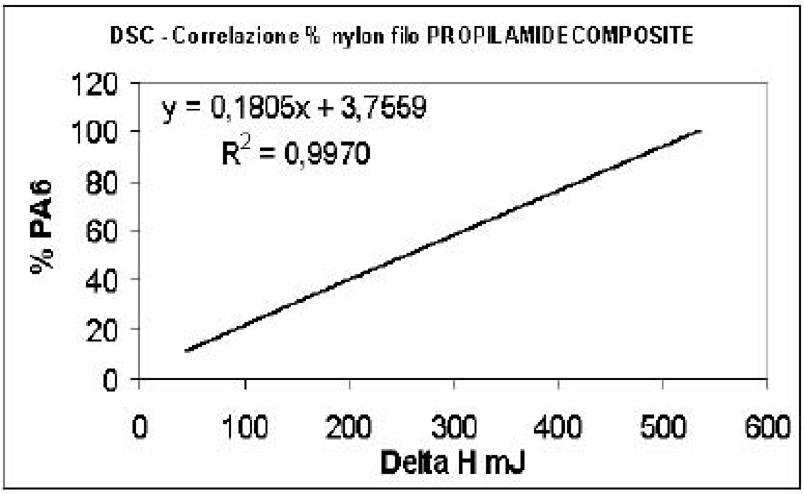


Fig.4 – DSC analysis of Propylamidecomposite fibers – Melting Enthalpy as a function of PA6wt%

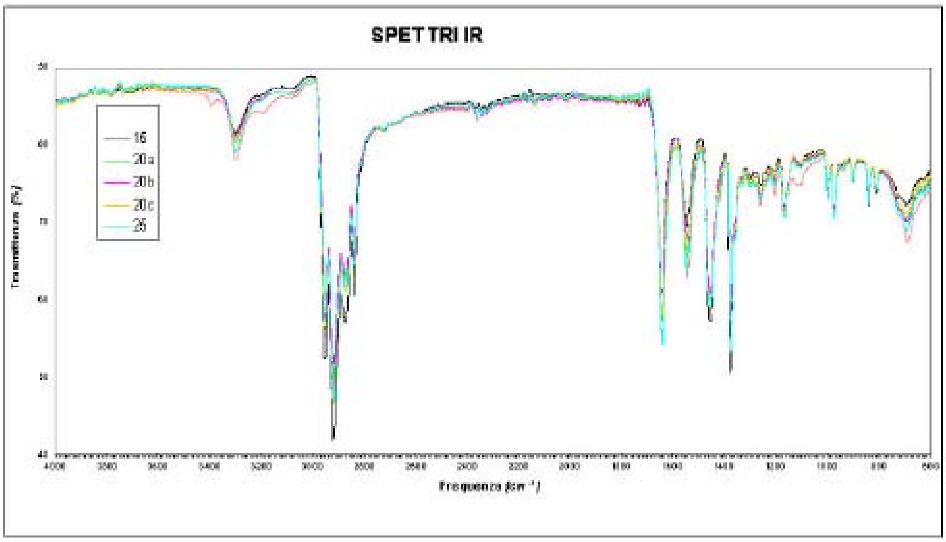


Figura 5.1: spettri IR

Fig.5 – FITR analysis of Propylamidecomposite fibers.

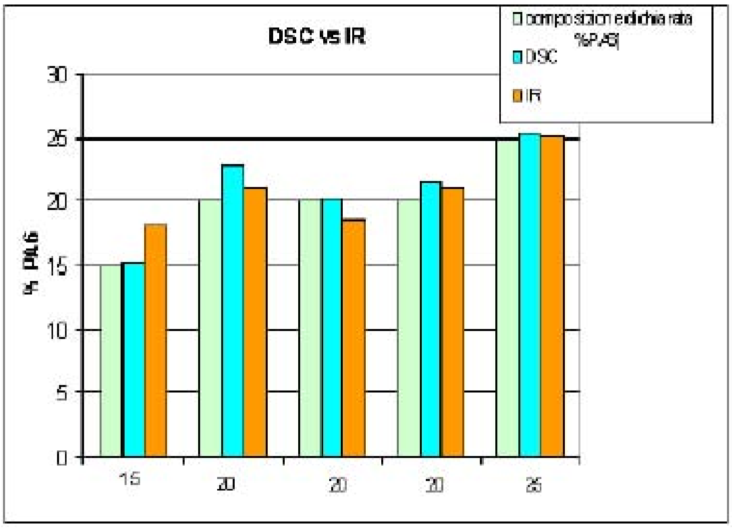


Grafico 5-6. scostamenti dalle percentuali dichiarate di PA6 con le due tecniche di analisi

Fig.6 – Comparison between Nominal PA6wt% content and results of DSC and FITR analysis of Propylamidecomposite fibers.

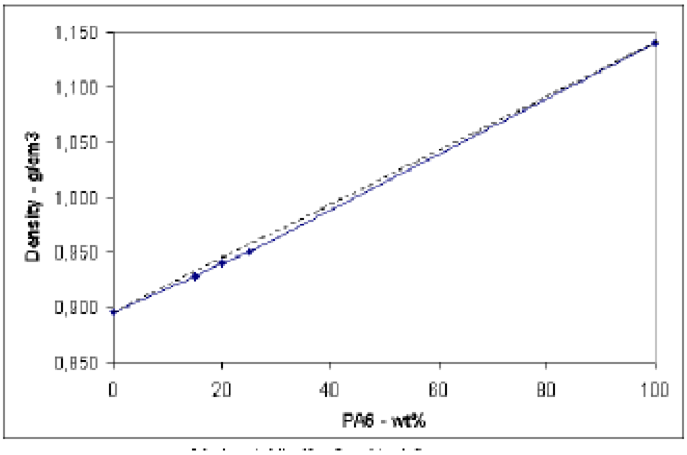


Fig.7 – Correlation between yarn density and nominal PA6 wt% content in Propylamidecomposite fibers. Dotted line represent a linear relationship.

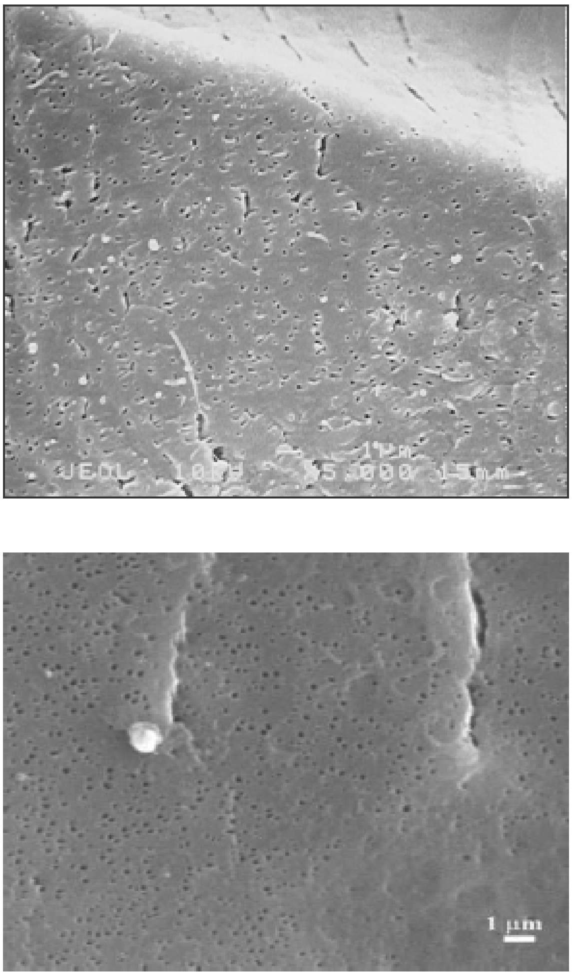


Fig.8 – Distribution of PA6 fibrils in the Propylamidecomposite fiber with 15wt% of PA6.

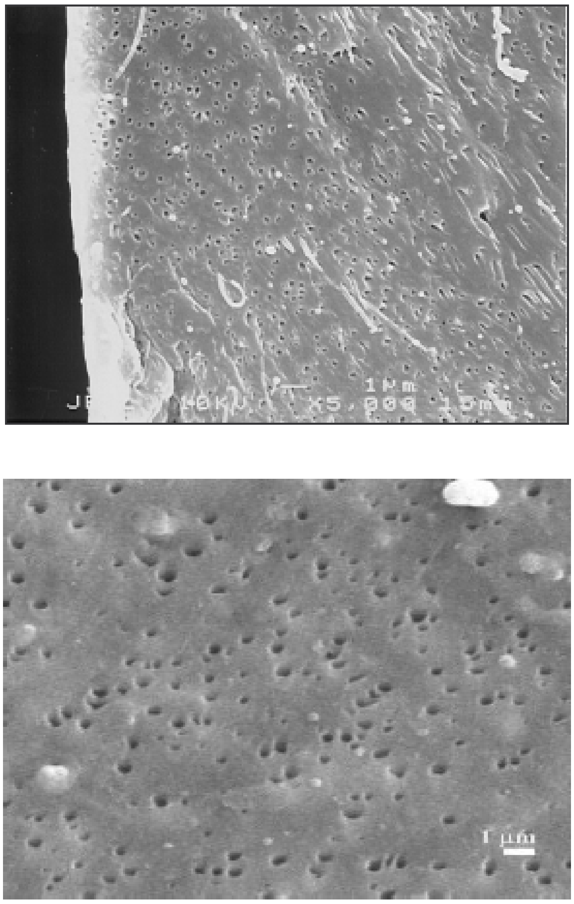


Fig.9 – Distribution of PA6 fibrils in the Propylamidecomposite fiber with 20wt% of PA6.

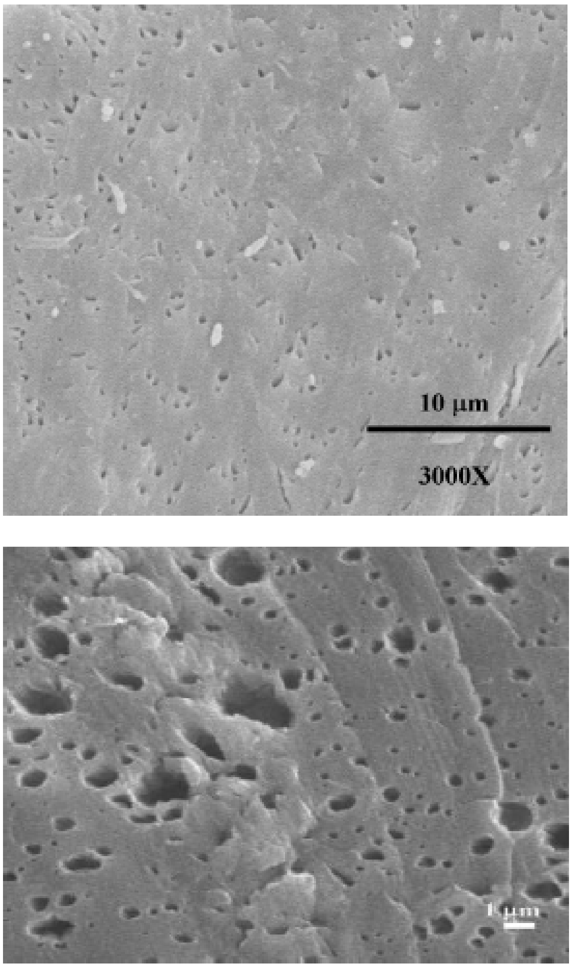


Fig.10 – Distribution of PA6 fibrils in the Propylamidecomposite fiber with 25wt% of PA6.

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Annex II

Microscopic analysis

polypropylene (sample 192)

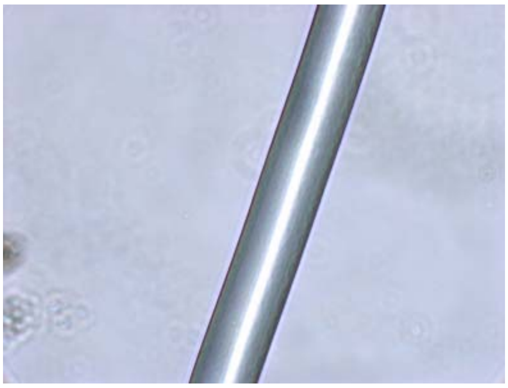

Fig. 1: Sample **192,** longitudinal view, 20X.

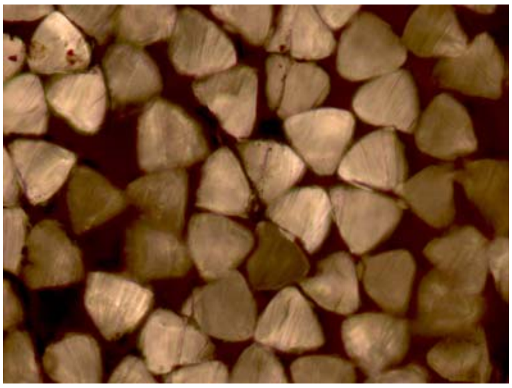

Fig. 2: Sample **192,** cross-section, 20X.

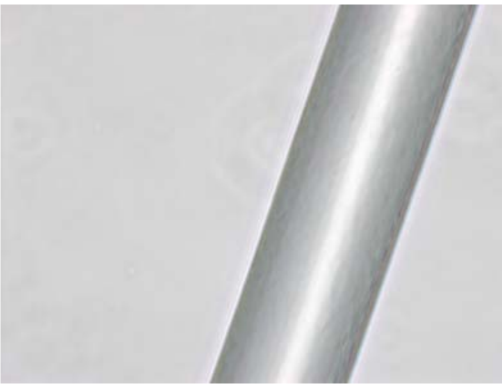

Fig. 3: Sample **192,** longitudinal view, 40X.

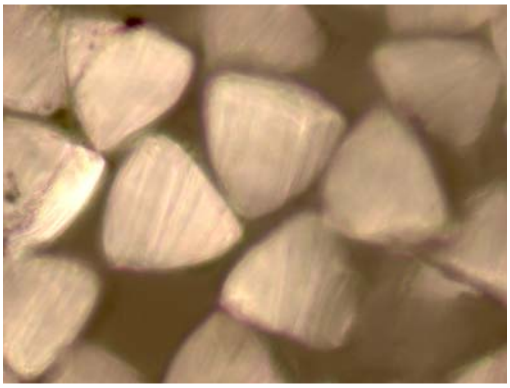

Fig. 4: Sample **192,** cross-section, 40X.

polyamide (sample 193)

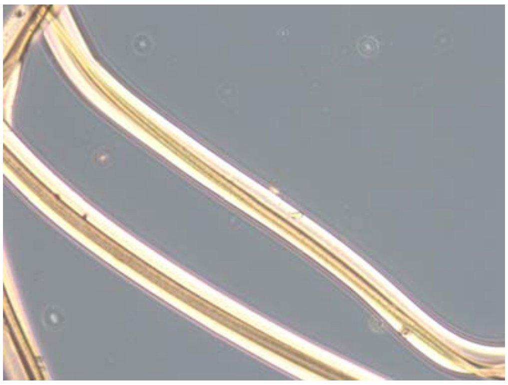

Fig. 5: Sample **193,** longitudinal view, 10X.

Fig. 6: Sample **193,** cross-section, 10X.

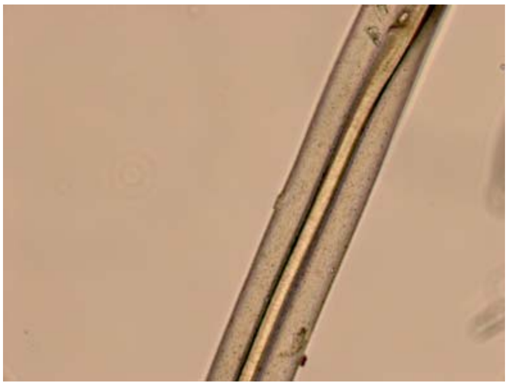

Fig. 7: Sample **193,** longitudinal view, 20X.

Fig. 8: Sample **193,** cross-section, 20X.

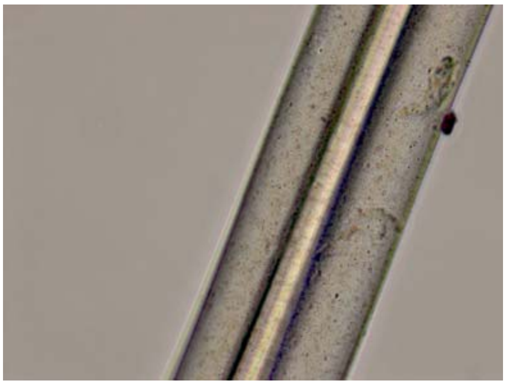

Fig.9: Sample **193,** longitudinal view, 40X.

Fig. 10: Sample **193,** cross-section, 40X.

PAC 40 % (sample 199)

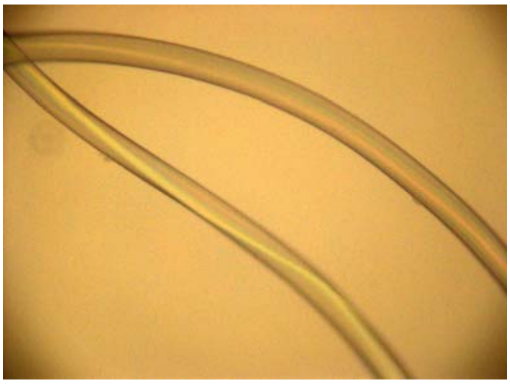

Fig.11: Sample **199,** longitudinal view, 10X.

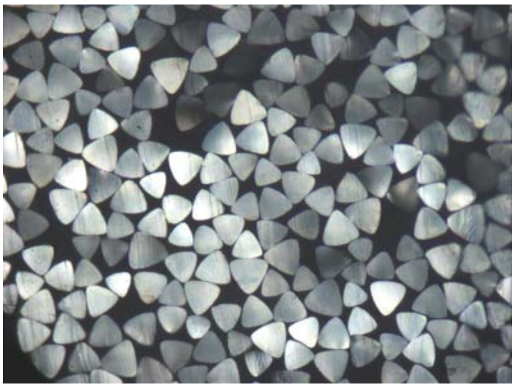

Fig. 12: Sample **199,** cross-section, 10X.

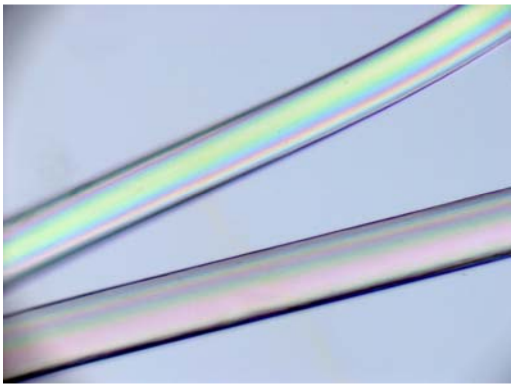

Fig.13: Sample **199,** longitudinal view, 20X.

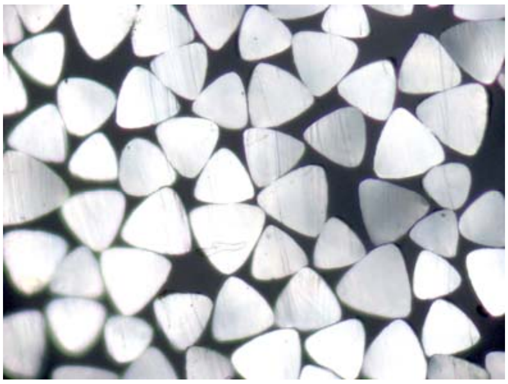

Fig. 14: Sample **199,** cross-section, 20X.

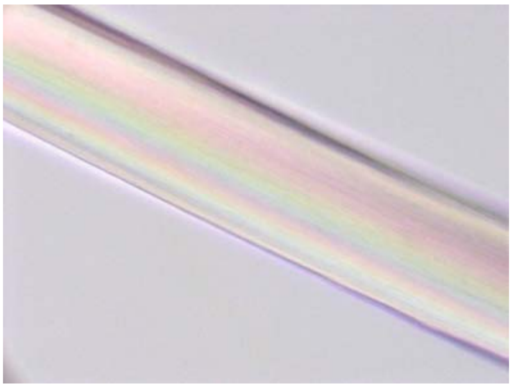

Fig.15: Sample **199,** longitudinal view, 40X.

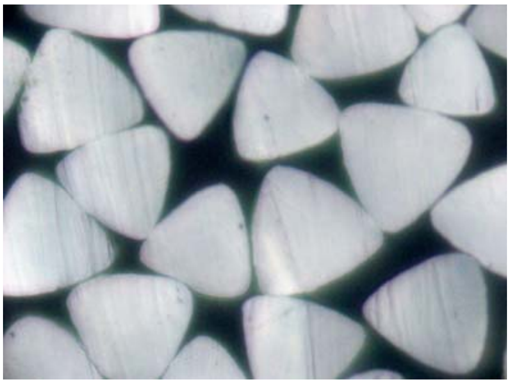

Fig. 16: Sample **199,** cross-section, 40X.

PA6/PAC 10% interlaced (sample 200)

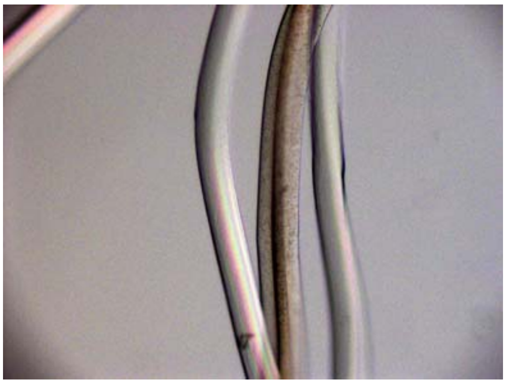

Fig.17: Sample **200,** longitudinal view, 10X.

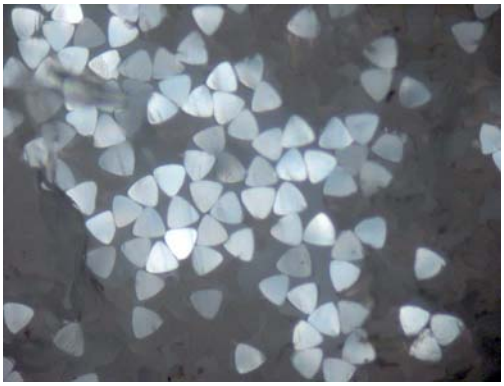

Fig. 18: Sample **200,** cross-section, 10X.

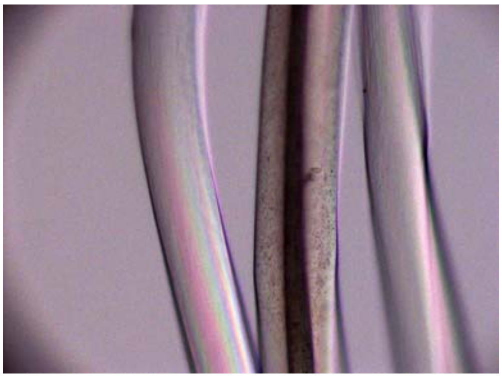

Fig.19: Sample **200,** longitudinal view, 20X.

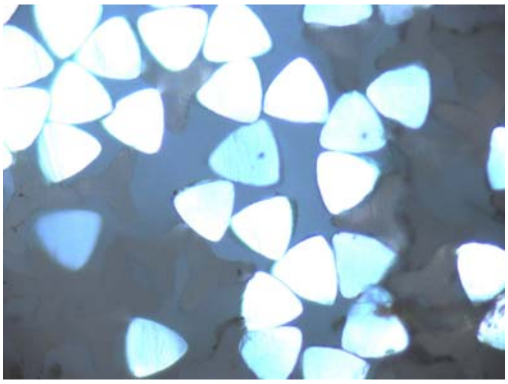

Fig. 20: Sample **200,** cross-section, 20X.

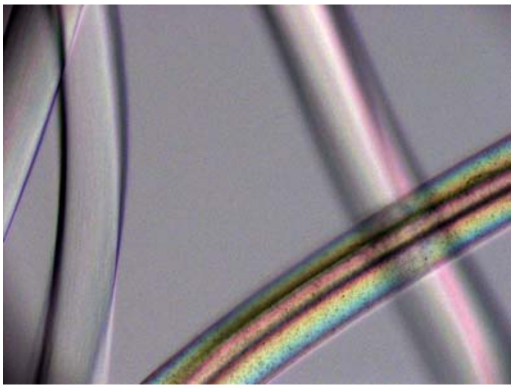

Fig.21: Sample **200,** longitudinal view, 40X.

Fig. 22: Sample **200,** cross-section, 40X.

PP/PAC 20% twisted (sample 210)

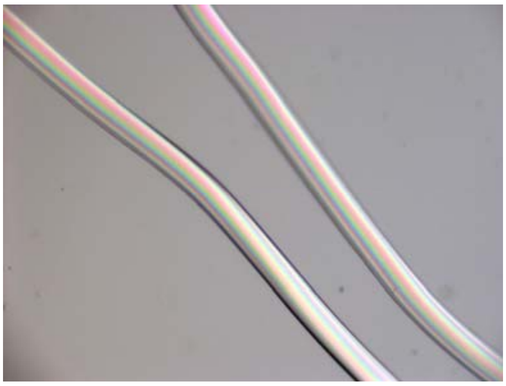

Fig.23: Sample **210,** longitudinal view, 10X.

Fig. 24: Sample **210,** cross-section, 20X.

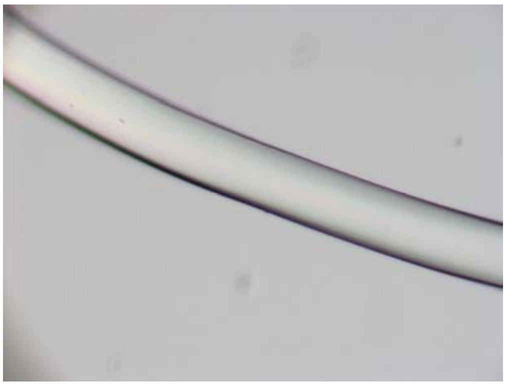

Fig. 25: Sample **210,** cross-section, 20X.

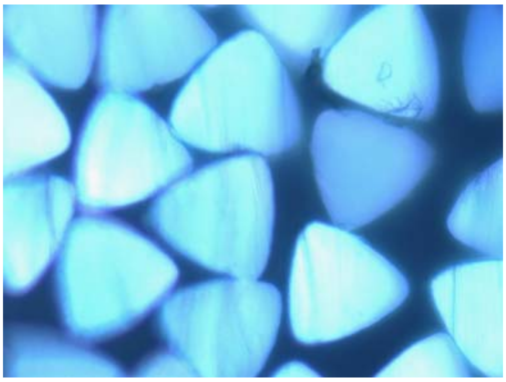

Fig. 26: Sample **210,** cross-section, 40X.

PP/PAC 20% twisted (sample 210)

Fig.27: Sample **210,** longitudinal view, 10X.

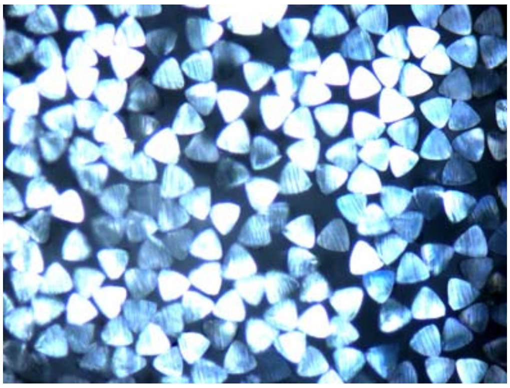

Fig. 28: Sample **210,** cross-section, 10X.

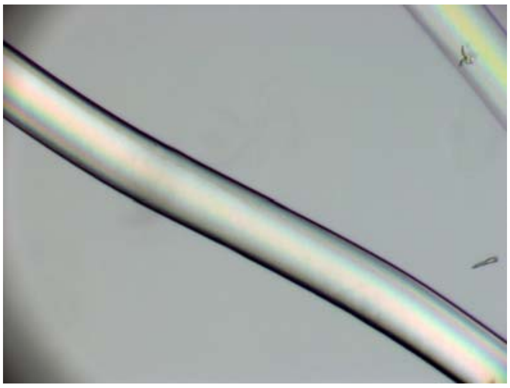

Fig.29: Sample **210,** longitudinal view, 20X.

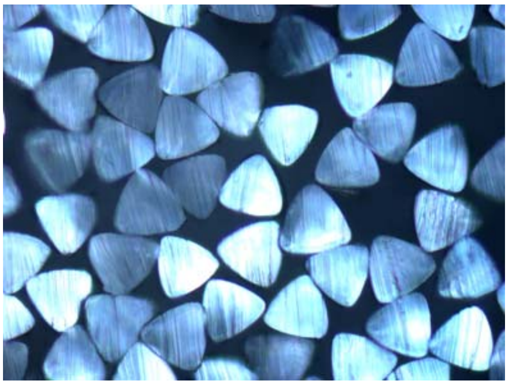

Fig. 30: Sample **210,** cross-section, 20X.

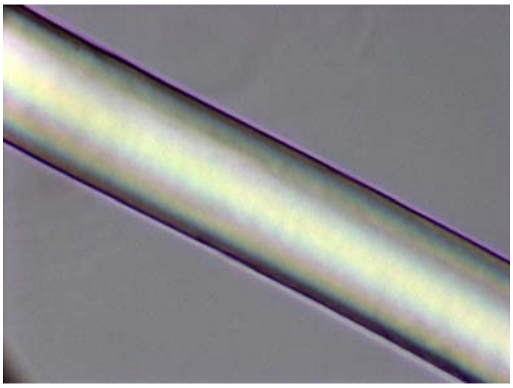

Fig.31: Sample **210,** longitudinal view, 40X.

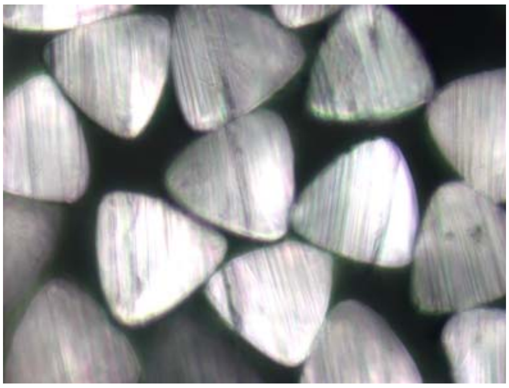

Fig. 32: Sample **210,** cross-section, 40X.

Annex III

Spectroscopic analysis FT-IR

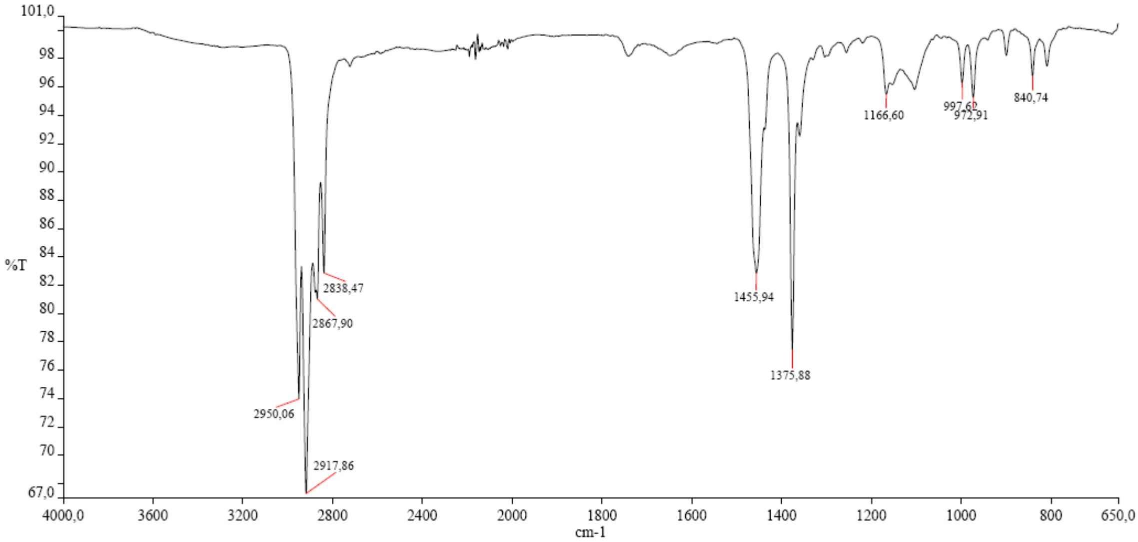

Fig. 1: FT-IR spectrum of polypropylene (sample **192**).

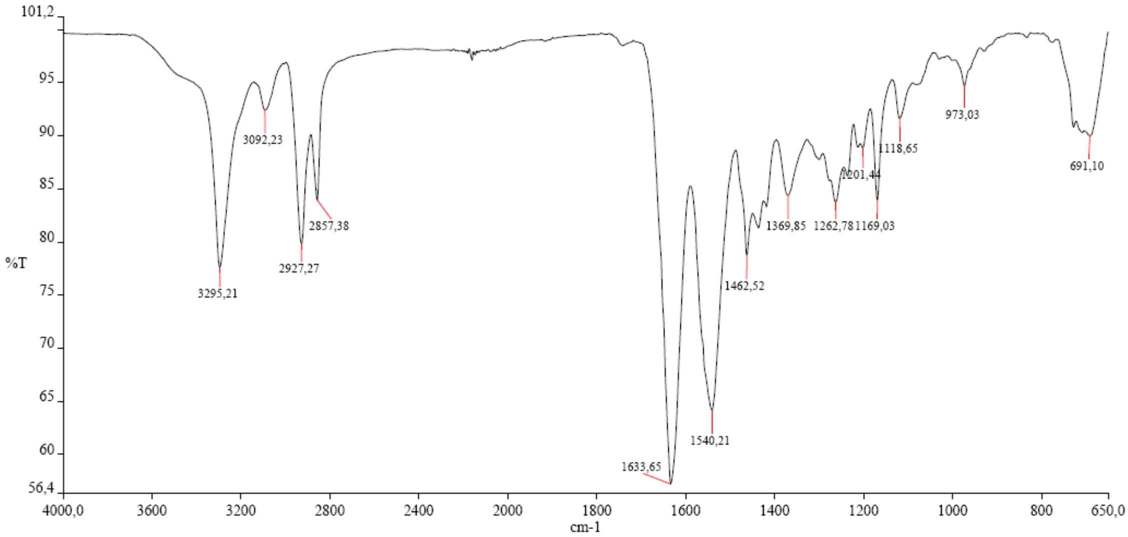

Fig. 2: FT-IR spectrum of polyamide 6 (sample **193**).

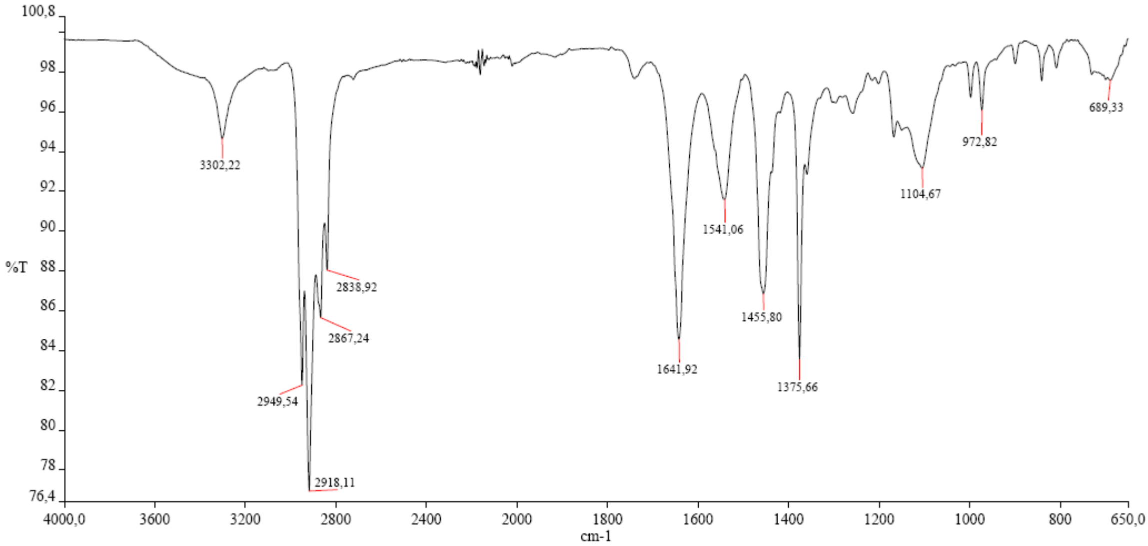

Fig. 3: FT-IR spectrum of PAC 20 % (sample **197**).

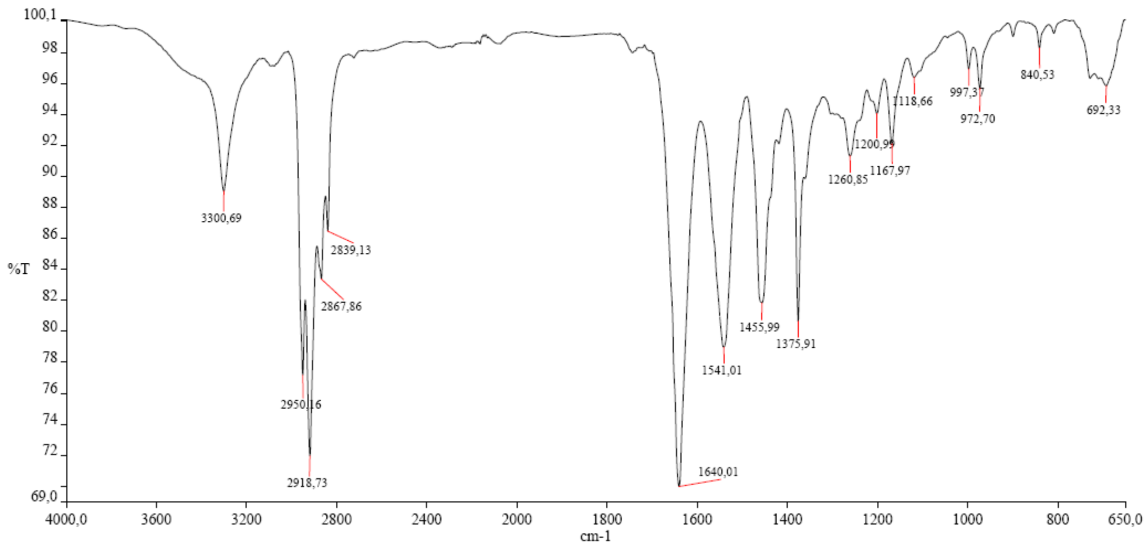

Fig. 4: FT-IR spectrum of PAC 40 % (sample **199**).

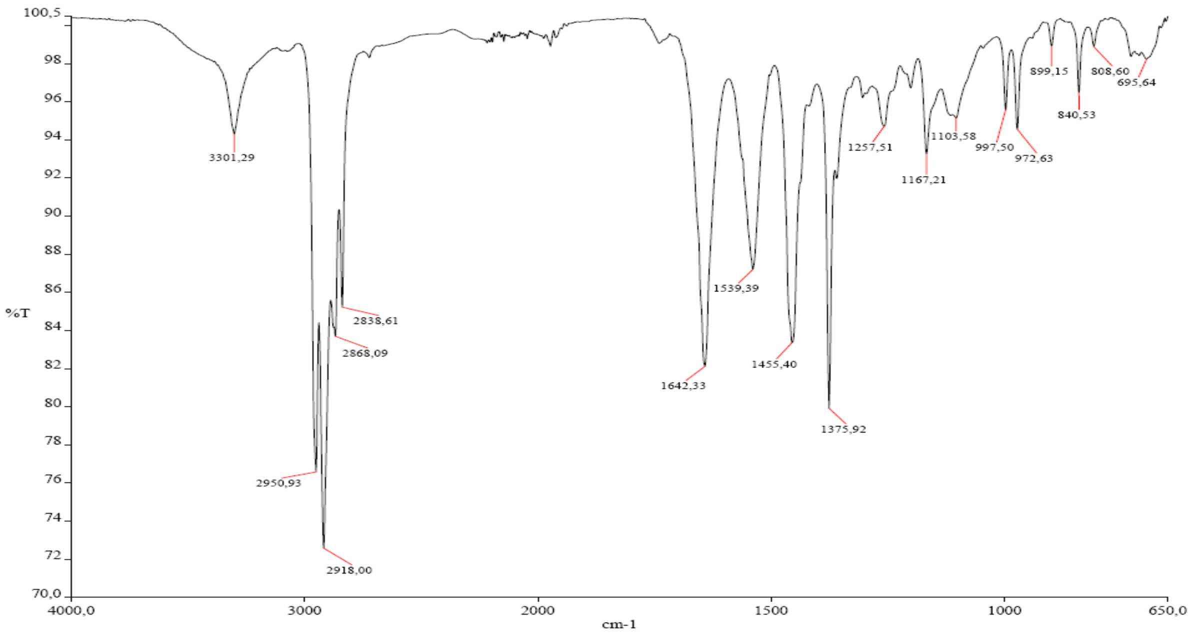

Fig. 5: FT-IR spectrum of PAC 20 % (sample **233**).

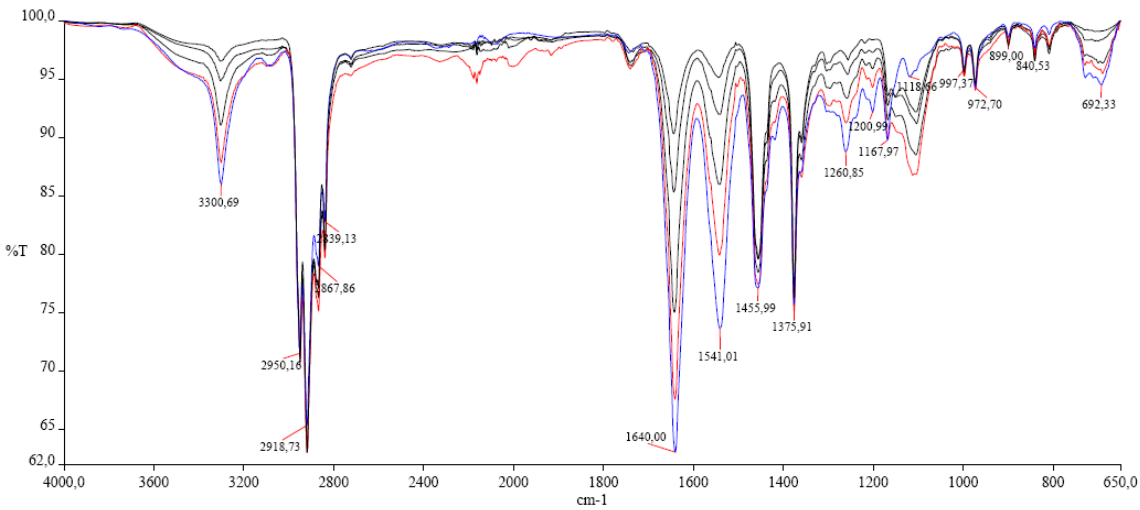

Fig. 6: Comparison of FT-IR spectra of PAC 5 % (---), 10 % (---), 20 % (---), 30 % (---), 40 % (---) (samples **195** - **199**).

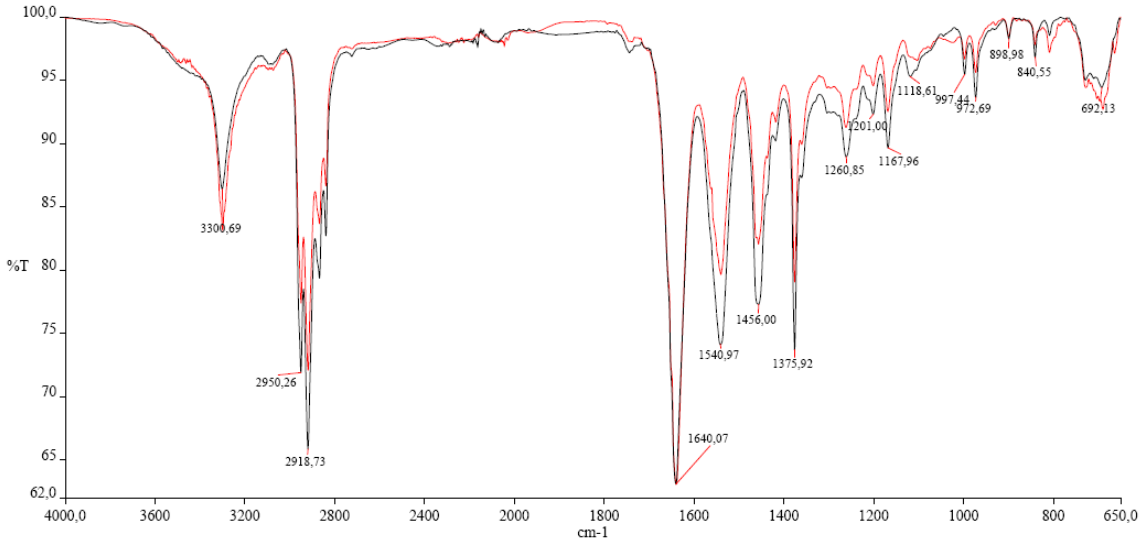

Fig. 7: Comparison of FT-IR spectra of untreated (---) and pre-treated (---) PAC 40 % (sample **199**).

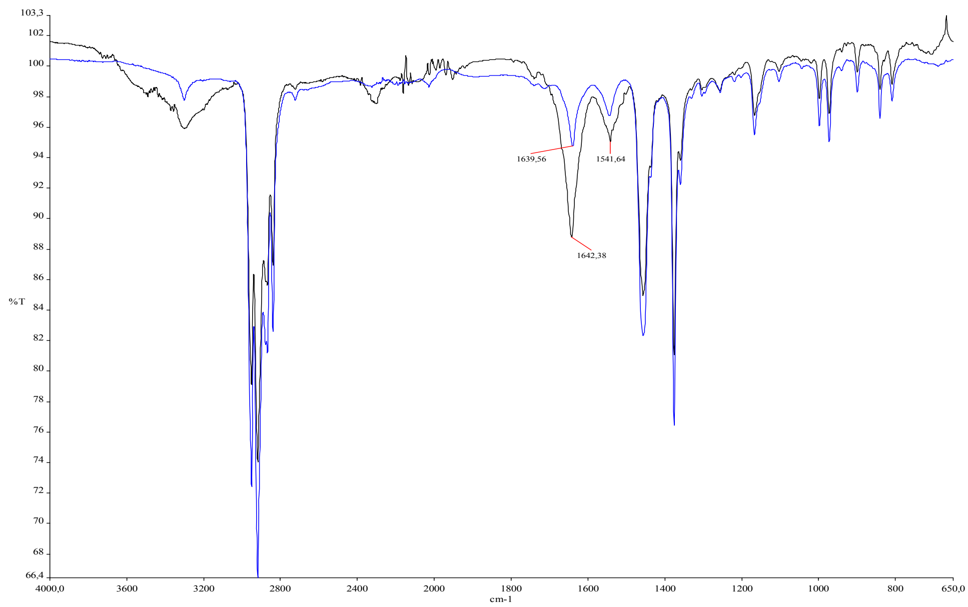

Fig. 8: Comparison of FT-IR spectra of PAC 20 % (sample **197**) as received (---) and after hydrolysis method (---).

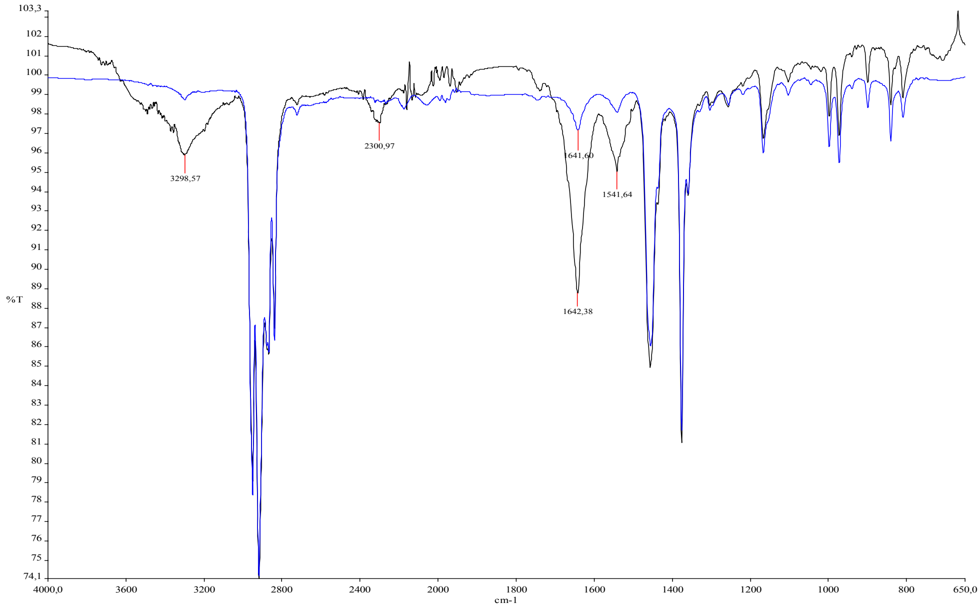

Fig. 9: Comparison of FT-IR spectra of PAC 20 % (sample **197**) as received (---) and after method 16 of Dir. 96/73/EC (---).

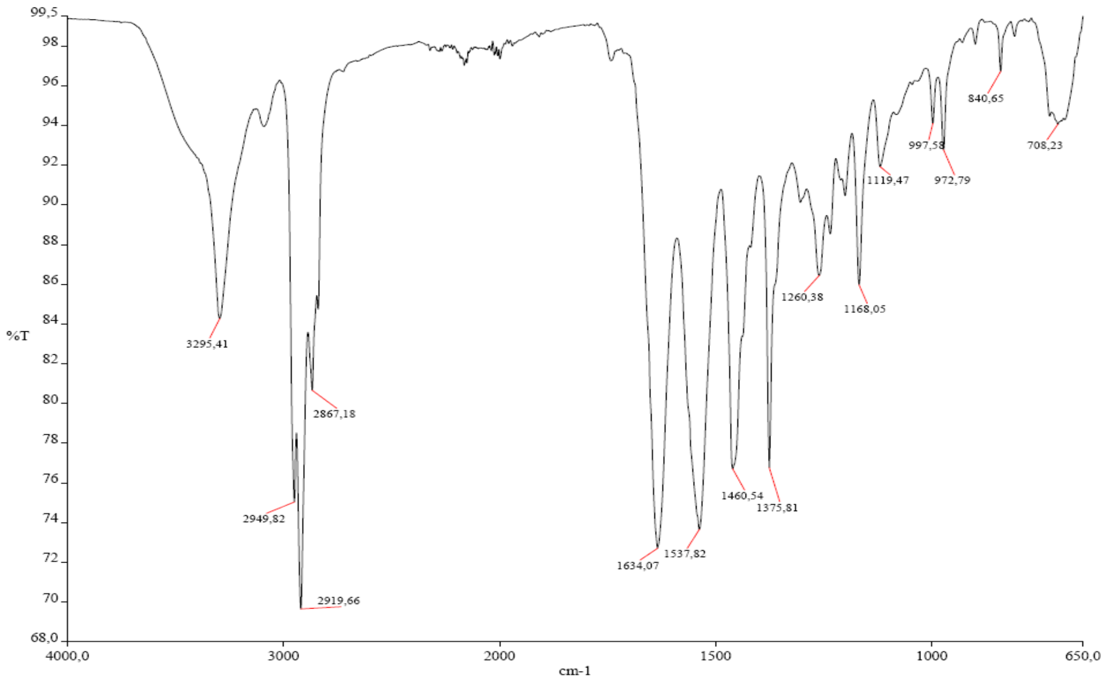

Fig. 10: FT-IR spectrum of “physical mixture” of PP and PA6 (PA6 content 20 %).

Annex IV

DSC analysis

Quantification of PA6 in PAC

PAC 5 %- 40 % (samples 195 - 199)

JRC code	PP peak area J/g	PA6 peak area J/g
195-1	104.60	3.60
195-2	104.30	3.52
195-3	103.30	3.56
average	**104.07**	**3.56**
confidence limit	**1.69**	**0.09**
SD	**0.68**	**0.04**
RSD %	**0.65**	**1.01**

JRC code	PP peak area J/g	PA6 peak area J/g
196-1	97.86	6.74
196-2	99.97	6.48
196-3	97.97	6.81
average	**98.60**	**6.67**
confidence limit	**2.95**	**0.43**
SD	**1.19**	**0.17**
RSD %	**1.20**	**2.62**

JRC code	PP peak area J/g	PA6 peak area J/g
197-1	90.61	12.27
197-2	88.02	12.21
197-3	87.31	11.96
average	**88.65**	**12.15**
confidence limit	**4.31**	**0.41**
SD	**1.74**	**0.16**
RSD %	**1.96**	**1.35**

JRC code	PP peak area J/g	PA6 peak area J/g
198-1	78.99	15.74
198-2	75.82	14.58
198-3	77.14	15.53
average	**77.32**	**15.28**
confidence limit	**3.96**	**1.54**
SD	**1.59**	**0.62**
RSD %	**2.06**	**4.04**

JRC code	PP peak area J/g	PA6 peak area J/g
199-1	65.71	20.91
199-2	65.91	19.18
199-3	64.24	18.22
average	**65.29**	**19.44**
confidence limit	**2.27**	**3.39**
SD	**0.91**	**1.36**
RSD %	**1.40**	**7.01**

Quantification of binary mixtures PA6/PAC

Binary mixtures PA6/PAC (samples 200 - 206)

JRC code	PP peak area J/g	PA6 peak area J/g
200-1	38.79	31.92
200-2	39.74	31.86
200-3	39.14	30.31
average	**39.22**	**31.36**
confidence limit	**1.19**	**2.27**
SD	**0.48**	**0.91**
RSD %	**1.22**	**2.91**

JRC code	PP peak area J/g	PA6 peak area J/g
201-1	38.22	33.14
201-2	38.79	32.26
201-3	38.93	32.72
average	**38.65**	**32.71**
confidence limit	**0.93**	**1.09**
SD	**0.38**	**0.44**
RSD %	**0.97**	**1.35**

JRC code	PP peak area J/g	PA6 peak area J/g
202-1	37.34	33.82
202-2	37.37	32.92
202-3	37.65	33.36
average	**37.45**	**33.37**
confidence limit	**0.42**	**1.12**
SD	**0.17**	**0.45**
RSD %	**0.46**	**1.35**

JRC code	PP peak area J/g	PA6 peak area J/g
203-1	37.38	34.51
203-2	37.07	34.76
203-3	36.85	34.73
average	**37.10**	**34.67**
confidence limit	**0.66**	**0.34**
SD	**0.27**	**0.14**
RSD %	**0.72**	**0.39**

JRC code	PP peak area J/g	PA6 peak area J/g
204-1	31.74	35.70
204-2	31.97	34.70
204-3	30.25	35.35
average	**31.32**	**35.25**
confidence limit	**2.32**	**1.26**
SD	**0.93**	**0.51**
RSD %	**2.98**	**1.44**

JRC code	PP peak area J/g	PA6 peak area J/g
205-1	31.87	36.71
205-2	30.18	34.59
205-3	32.01	36.21
average	**31.35**	**35.84**
confidence limit	**2.53**	**2.75**
SD	**1.02**	**1.11**
RSD %	**3.25**	**3.09**

JRC code	PP peak area J/g	PA6 peak area J/g
206-1	30.09	37.91
206-2	28.12	37.10
206-3	27.95	38.06
average	**28.72**	**37.69**
confidence limit	**2.95**	**1.28**
SD	**1.19**	**0.52**
RSD %	**4.14**	**1.37**

Quantification of binary mixtures PP/PAC

Binary mixtures PP/PAC (samples 207 - 213)

JRC code	PP peak area J/g	PA6 peak area J/g
207-1	100.1	3.15
207-2	99.71	3.18
average	**99.91**	**3.16**
confidence limit	**2.48**	**0.14**
SD	**0.28**	**0.02**
RSD %	**0.28**	**0.49**

JRC code	PP peak area J/g	PA6 peak area J/g
208-1	97.92	3.17
208-2	98.13	3.25
208-3	96.91	3.10
average	**97.65**	**3.17**
confidence limit	**1.62**	**0.18**
SD	**0.65**	**0.07**
RSD %	**0.67**	**2.32**

JRC code	PP peak area J/g	PA6 peak area J/g
209-1	92.15	5.36
209-2	93.46	5.29
209-3	94.74	5.66
average	**93.45**	**5.44**
confidence limit	**3.22**	**0.50**
SD	**1.30**	**0.20**
RSD %	**1.39**	**3.67**

JRC code	PP peak area J/g	PA6 peak area J/g
210-1	94.74	5.42
210-2	94.72	5.29
210-3	93.78	5.12
average	**94.41**	**5.28**
confidence limit	**1.36**	**0.37**
SD	**0.55**	**0.15**
RSD %	**0.58**	**2.79**

JRC code	PP peak area J/g	PA6 peak area J/g
211-1	94.56	7.63
211-2	94.78	7.32
211-3	95.26	7.53
average	**94.87**	**7.49**
confidence limit	**0.89**	**0.40**
SD	**0.36**	**0.16**
RSD %	**0.38**	**2.15**

JRC code	PP peak area J/g	PA6 peak area J/g
212-1	93.55	7.52
212-2	94.74	7.13
212-3	95.87	7.58
average	**94.72**	**7.41**
confidence limit	**2.88**	**0.60**
SD	**1.16**	**0.24**
RSD %	**1.22**	**3.28**

JRC code	PP peak area J/g	PA6 peak area J/g
213-1	88.07	9.36
213-2	90.88	10.97
213-3		9.53
average	**89.48**	**9.95**
confidence limit	**17.85**	**2.20**
SD	**1.99**	**0.88**
RSD %	**2.22**	**8.89**

Annex V

Analysis of composition

Influence of drying conditions on PAC

PAC 20 % (samples 160, 197, 233)

- ***Vacuum oven***

JRC code	time h	wet sample mass g	dried sample mass g	water mass g	loss of mass %
160-1	2	6.0344	5.9888	0.0456	**0.756**
160-2	4	6.0652	6.0183	0.0469	**0.773**
160-3	6	6.0312	5.9874	0.0438	**0.726**
160-4	8	6.0622	6.0199	0.0423	**0.698**
160-5	12	6.0593	6.0139	0.0454	**0.749**
160-6	16	5.9671	5.9269	0.0402	**0.674**

JRC code	time h	wet sample mass g	dried sample mass g	water mass g	loss of mass %
197-1	2	6.2282	6.1795	0.0487	**0.782**
197-2	4	6.2273	6.1776	0.0497	**0.798**
197-3	6	6.2449	6.1980	0.0469	**0.751**
197-4	8	6.2196	6.1770	0.0426	**0.685**
197-5	12	6.2647	6.2180	0.0467	**0.745**
197-6	16	6.2667	6.2258	0.0409	**0.653**

JRC code	time h	wet sample mass g	dried sample mass g	water mass g	loss of mass %
233-1	2	6.1383	6.0893	0.0490	**0.798**
233-2	4	6.1913	6.1414	0.0499	**0.806**
233-3	6	6.2964	6.2502	0.0462	**0.734**
233-4	8	6.2040	6.1598	0.0442	**0.712**
233-5	12	6.1510	6.1055	0.0455	**0.740**
233-6	16	6.2927	6.2494	0.0433	**0.688**

- ***Ventilated oven***

JRC code	time h	wet sample mass g	dried sample mass g	water mass g	loss of mass %
160-1	2	6.0376	5.9923	0.0453	**0.750**
160-2	4	6.1139	6.0662	0.0477	**0.780**
160-3	6	6.1657	6.1397	0.0260	**0.422**
160-4	8	6.0477	6.0274	0.0203	**0.336**
160-5	12	6.0327	5.9930	0.0397	**0.658**
160-6	16	6.0460	6.0012	0.0448	**0.741**

JRC code	time h	wet sample mass g	dried sample mass g	water mass g	loss of mass %
197-1	2	6.1665	6.1185	0.0480	**0.778**
197-2	4	6.1669	6.1171	0.0498	**0.808**
197-3	6	6.1758	6.1305	0.0453	**0.734**
197-4	8	6.2624	6.2159	0.0465	**0.743**
197-5	12	6.2312	6.1843	0.0469	**0.753**
197-6	16	6.2221	6.1799	0.0422	**0.678**

JRC code	time h	wet sample mass g	dried sample mass g	water mass g	loss of mass %
233-1	2	6.2140	6.1673	0.0467	**0.752**
233-2	4	6.2281	6.1801	0.0480	**0.771**
233-3	6	6.1681	6.1234	0.0447	**0.725**
233-4	8	6.1876	6.1425	0.0451	**0.729**
233-5	12	6.2630	6.2138	0.0492	**0.786**
233-6	16	6.1941	6.1494	0.0447	**0.722**

Pre-treatment with petroleum ether in Soxhtec

polypropylene (sample 192)

JRC code	untreated sample mass g	pre-treated sample mass g	mass loss g	mass loss %
192-1	5.3461	5.2875	0.0586	1.10
192-2	5.4132	5.3560	0.0572	1.06
192-3	5.3385	5.2795	0.0590	1.11
192-4	5.4301	5.3715	0.0586	1.08
192-5	5.4412	5.3812	0.0600	1.10
			average	1.09
			confidence limit	0.03
			SD	0.02
			RSD %	1.86

polyamide 6 (sample 193)

JRC code	untreated sample mass g	pre-treated sample mass g	mass loss g	mass loss %
193-1	5.4018	5.3505	0.0513	0.95
193-2	5.5224	5.4651	0.0573	1.04
193-3	5.4091	5.3565	0.0526	0.97
193-4	5.4931	5.4294	0.0637	1.16
193-5	5.4590	5.3999	0.0591	1.08
			average	1.04
			confidence limit	0.11
			SD	0.08
			RSD %	8.16

PAC (samples 195 - 199, 233)

JRC code	untreated sample mass g	pre-treated sample mass g	mass loss g	mass loss %
195-1	5.2184	5.1623	0.0561	1.08
195-2	5.2198	5.1608	0.0590	1.13
195-3	5.1947	5.1363	0.0584	1.12
195-4	5.2911	5.2336	0.0575	1.09
195-5	5.2066	5.1520	0.0546	1.05
			average	1.09
			confidence limit	0.04
			SD	0.03
			RSD %	3.13

JRC code	untreated sample mass g	pre-treated sample mass g	mass loss g	mass loss %
196-1	5.2086	5.1531	0.0555	1.07
196-2	5.1682	5.1136	0.0546	1.06
196-3	5.1901	5.1359	0.0542	1.04
196-4	5.1947	5.1387	0.0560	1.08
196-5	5.2093	5.1565	0.0528	1.01
			average	1.05
			confidence limit	0.03
			SD	0.02
			RSD %	2.34

JRC code	untreated sample mass g	pre-treated sample mass g	mass loss g	mass loss %
197-1	5.2394	5.1839	0.0555	1.06
197-2	5.2509	5.1970	0.0539	1.03
197-3	5.1916	5.1343	0.0573	1.10
197-4	5.2236	5.1692	0.0544	1.04
197-5	5.2798	5.2235	0.0563	1.07
			average	**1.06**
			confidence limit	**0.04**
			SD	**0.03**
			RSD %	**2.76**

JRC code	untreated sample mass g	pre-treated sample mass g	mass loss g	mass loss %
198-1	5.3072	5.2494	0.0578	1.09
198-2	5.3004	5.2418	0.0586	1.11
198-3	5.3708	5.3151	0.0557	1.04
198-4	5.2525	5.1950	0.0575	1.09
198-5	5.3384	5.2829	0.0555	1.04
			average	**1.07**
			confidence limit	**0.04**
			SD	**0.03**
			RSD %	**3.02**

JRC code	untreated sample mass g	pre-treated sample mass g	mass loss g	mass loss %
199-1	5.2242	5.1772	0.0470	0.90
199-2	5.3317	5.2821	0.0496	0.93
199-3	5.2822	5.2327	0.0495	0.94
199-4	5.356	5.3047	0.0513	0.96
199-5	5.3517	5.3003	0.0514	0.96
			average	**0.94**
			confidence limit	**0.03**
			SD	**0.02**
			RSD %	**2.63**

1st pre-treatment

JRC code	untreated sample mass	pre-treated sample mass	mass loss	mass loss
	g	g	g	%
233-1	4.8803	4.8352	0.0451	0.92
233-2	4.9304	4.8815	0.0489	0.99
233-3	4.9396	4.8923	0.0473	0.96
233-4	5.3062	5.2558	0.0504	0.95
233-5	4.9809	4.9344	0.0465	0.93
			average	0.95
			confidence limit	0.03
			SD	0.03
			RSD %	2.75

2nd pre-treatment

JRC code	untreated sample mass	pre-treated sample mass	mass loss	mass loss
	g	g	g	%
233-1	4.8352	4.8281	0.0071	0.15
233-2	4.8815	4.8750	0.0065	0.13
233-3	4.8923	4.8855	0.0068	0.14
233-4	5.2558	5.2482	0.0076	0.14
233-5	4.9344	4.9264	0.0080	0.16
			average	0.15
			confidence limit	0.01
			SD	0.01
			RSD %	7.49

3rd pre-treatment

JRC code	untreated sample mass	pre-treated sample mass	mass loss	mass loss
	g	g	g	%
233-1	4.8281	4.8233	0.0048	0.10
233-2	4.8750	4.8689	0.0061	0.13
233-3	4.8855	4.8806	0.0049	0.10
233-4	5.2482	5.2425	0.0057	0.11
233-5	4.9264	4.9193	0.0071	0.14
			average	0.12
			confidence limit	0.02
			SD	0.02
			RSD %	16.48

Agreed allowance

untreated PAC 5 %– 40 % (samples 195 - 199)

JRC code	dried sample mass g	wet sample mass g	water mass g	agreed allowance %
195-1	2.0641	2.0673	0.0032	0.16
195-2	2.0713	2.0744	0.0031	0.15
195-3	2.0732	2.0758	0.0026	0.13
195-4	2.045	2.0483	0.0033	0.16
195-5	2.0465	2.0491	0.0026	0.13
195-6	2.0499	2.0532	0.0033	0.16
195-7	2.0202	2.0225	0.0023	0.11
195-8	2.0135	2.0169	0.0034	0.17
195-9	2.0615	2.0648	0.0033	0.16
195-10	2.0446	2.0479	0.0033	0.16
			average	**0.15**
			confidence limit	**0.01**
			SD	**0.02**
			RSD %	**12.86**

JRC code	dried sample mass g	wet sample mass g	water mass g	agreed allowance %
196-1	2.0885	2.0949	0.0064	0.31
196-2	2.0578	2.0637	0.0059	0.29
196-3	2.0608	2.0671	0.0063	0.31
196-4	2.0803	2.0862	0.0059	0.28
196-5	2.0821	2.0882	0.0061	0.29
196-6	2.0235	2.0297	0.0062	0.31
196-7	2.0587	2.0644	0.0057	0.28
196-8	1.7843	1.7891	0.0048	0.27
196-9	2.0284	2.0341	0.0057	0.28
196-10	2.0049	2.0108	0.0059	0.29
			average	**0.29**
			confidence limit	**0.01**
			SD	**0.01**
			RSD %	**4.53**

JRC code	dried sample mass g	wet sample mass g	water mass g	agreed allowance %
197-1	2.0448	2.0568	0.0120	0.59
197-2	2.0718	2.0835	0.0117	0.56
197-3	2.025	2.0375	0.0125	0.62
197-4	2.0412	2.0517	0.0105	0.51
197-5	2.0372	2.0482	0.0110	0.54
197-6	2.0698	2.0814	0.0116	0.56
197-7	2.0175	2.0288	0.0113	0.56
197-8	2.019	2.0301	0.0111	0.55
197-9	2.0581	2.0696	0.0115	0.56
197-10	2.047	2.0583	0.0113	0.55
			average	**0.56**
			confidence limit	**0.02**
			SD	**0.03**
			RSD %	**4.86**

JRC code	dried sample mass g	wet sample mass g	water mass g	agreed allowance %
198-1	2.0176	2.0362	0.0186	0.92
198-2	2.0105	2.0286	0.0181	0.90
198-3	2.0332	2.0505	0.0173	0.85
198-4	2.0107	2.0276	0.0169	0.84
198-5	2.0726	2.0903	0.0177	0.85
198-6	2.0145	2.0323	0.0178	0.88
198-7	2.031	2.0493	0.0183	0.90
198-8	2.0714	2.0910	0.0196	0.95
198-9	2.0453	2.0626	0.0173	0.85
198-10	2.0193	2.0362	0.0169	0.84
			average	**0.88**
			confidence limit	**0.03**
			SD	**0.04**
			RSD %	**4.34**

JRC code	dried sample mass g	wet sample mass g	water mass g	agreed allowance %
199-1	2.0519	2.0765	0.0246	1.20
199-2	2.0368	2.0608	0.0240	1.18
199-3	2.0203	2.0450	0.0247	1.22
199-4	2.0719	2.0945	0.0226	1.09
199-5	2.0462	2.0691	0.0229	1.12
199-6	2.0279	2.0499	0.0220	1.08
199-7	2.0627	2.0858	0.0231	1.12
199-8	1.9965	2.0190	0.0225	1.13
199-9	2.0389	2.0623	0.0234	1.15
199-10	2.0564	2.0809	0.0245	1.19
			average	**1.15**
			confidence limit	**0.03**
			SD	**0.05**
			RSD %	**4.13**

pre-treated PAC 5 %– 40 % (samples 195 - 199)

JRC code	dried sample mass g	wet sample mass g	water mass g	agreed allowance %
195-1	2.0139	2.0148	0.0009	0.04
195-2	2.0710	2.0719	0.0009	0.04
195-3	2.0517	2.0531	0.0014	0.07
195-4	2.0338	2.0358	0.0020	0.10
195-5	2.0219	2.0234	0.0015	0.07
195-6	2.0627	2.0637	0.0010	0.05
195-7	2.0300	2.0317	0.0017	0.08
195-8	2.0453	2.0478	0.0025	0.12
195-9	2.0200	2.0241	0.0041	0.20
195-10	2.0152	2.0168	0.0016	0.08
			average	**0.09**
			confidence limit	**0.03**
			SD	**0.05**
			RSD %	**55.22**

JRC code	dried sample mass g	wet sample mass g	water mass g	agreed allowance %
196-1	2.0535	2.0586	0.0051	0.25
196-2	2.0557	2.0604	0.0047	0.23
196-3	2.0255	2.0305	0.0050	0.25
196-4	2.0175	2.0201	0.0026	0.13
196-5	2.0256	2.0309	0.0053	0.26
196-6	2.0458	2.0524	0.0066	0.32
196-7	2.0215	2.0260	0.0045	0.22
196-8	2.0309	2.0367	0.0058	0.29
196-9	2.0131	2.0177	0.0046	0.23
196-10	2.0704	2.0716	0.0012	0.06
			average	**0.22**
			confidence limit	**0.05**
			SD	**0.08**
			RSD %	**34.29**

JRC code	dried sample mass g	wet sample mass g	water mass g	agreed allowance %
197-1	2.0375	2.0489	0.0114	0.56
197-2	2.0358	2.0478	0.0120	0.59
197-3	2.0196	2.0293	0.0097	0.48
197-4	2.0684	2.0796	0.0112	0.54
197-5	2.0256	2.0369	0.0113	0.56
197-6	2.0425	2.0526	0.0101	0.49
197-7	2.0760	2.0851	0.0091	0.44
197-8	2.0532	2.0653	0.0121	0.59
197-9	2.0054	2.0151	0.0097	0.48
197-10	2.0629	2.0734	0.0105	0.51
			average	**0.52**
			confidence limit	**0.04**
			SD	**0.05**
			RSD %	**9.69**

JRC code	dried sample mass g	wet sample mass g	water mass g	agreed allowance %
198-1	2.0508	2.0673	0.0165	0.80
198-2	2.0504	2.0631	0.0127	0.62
198-3	2.0006	2.0179	0.0173	0.86
198-4	2.0101	2.0277	0.0176	0.88
198-5	2.0473	2.0644	0.0171	0.84
198-6	2.0045	2.0188	0.0143	0.71
198-7	2.0051	2.0206	0.0155	0.77
198-8	2.0162	2.0344	0.0182	0.90
198-9	2.0145	2.0298	0.0153	0.76
198-10	2.0184	2.0327	0.0143	0.71
			average	**0.79**
			confidence limit	**0.06**
			SD	**0.09**
			RSD %	**11.27**

JRC code	dried sample mass g	wet sample mass g	water mass g	agreed allowance %
199-1	2.0149	2.0391	0.0242	1.20
199-2	2.0292	2.0522	0.0230	1.13
199-3	2.0470	2.0702	0.0232	1.13
199-4	2.0279	2.0495	0.0216	1.07
199-5	2.0283	2.0505	0.0222	1.09
199-6	2.0313	2.0551	0.0238	1.17
199-7	2.0202	2.0438	0.0236	1.17
199-8	2.0206	2.0444	0.0238	1.18
199-9	2.0231	2.0461	0.0230	1.14
199-10	2.0122	2.0342	0.0220	1.09
			average	**1.14**
			confidence limit	**0.03**
			SD	**0.04**
			RSD %	**3.80**

Influence of drying conditions on solubility properties of PAC

PAC 20 % (sample 233)

- ***Vacuum oven***

Method 1

JRC code	sample mass g	residue mass g	PAC %	soluble %	d
233-1	1.0382	1.0401	100.18	-0.18	0.998
233-2	1.1399	1.1411	100.10	-0.10	0.999
233-3	1.1219	1.1250	100.27	-0.27	0.997
233-4	1.0750	1.0723	99.75	0.25	1.003
233-5	1.1982	1.2100	100.97	-0.97	0.990
		average	**100.26**	**-0.26**	**0.997**
		confidence limit	**0.56**	**0.56**	**0.006**
		SD	**0.45**	**0.45**	**0.004**
		RSD %	**0.45**	**-174.03**	**0.449**

Method 2

JRC code	sample mass g	residue mass g	PAC %	soluble %	d
233-1	0.9978	0.9973	99.95	0.05	1.001
233-2	1.0178	1.0169	99.91	0.09	1.001
233-3	1.0466	1.0474	100.08	-0.08	0.999
233-4	1.0005	1.0028	100.23	-0.23	0.998
233-5	1.0350	1.0327	99.78	0.22	1.002
		average	**99.99**	**0.01**	**1.000**
		confidence limit	**0.21**	**0.21**	**0.002**
		SD	**0.17**	**0.17**	**0.002**
		RSD %	**0.17**	**1576.00**	**0.172**

Method 5

JRC code	sample mass g	residue mass g	PAC %	soluble %	d
233-1	0.9736	0.9746	100.10	-0.10	0.999
233-2	1.0043	1.0037	99.94	0.06	1.001
233-3	0.9967	1.0065	100.97	-0.97	0.990
233-4	1.0482	1.0578	100.91	-0.91	0.991
233-5	0.9977	1.0021	100.44	-0.44	0.996
		average	**100.47**	**-0.47**	**0.995**
		confidence limit	**0.58**	**0.58**	**0.006**
		SD	**0.46**	**0.46**	**0.005**
		RSD %	**0.46**	**-98.32**	**0.466**

Method 6

JRC code	sample mass g	residue mass g	PAC %	soluble %	d
233-1	1.0235	1.0195	99.61	0.39	1.004
233-2	1.0284	1.0298	100.13	-0.13	0.999
233-3	1.0369	1.0373	100.04	-0.04	1.000
233-4	1.0220	1.0220	100.00	0.00	1.000
233-5	1.0106	1.0126	100.20	-0.20	0.998
		average	**100.00**	**0.00**	**1.000**
		confidence limit	**0.28**	**0.28**	**0.003**
		SD	**0.23**	**0.23**	**0.002**
		RSD %	**0.23**	**6314.24**	**0.231**

Method 8

JRC code	sample mass g	residue mass g	PAC %	soluble %	d
233-1	1.0647	1.0631	99.85	0.15	1.002
233-2	1.0116	1.0128	100.12	-0.12	0.999
233-3	1.0423	1.0423	100.00	0.00	1.000
233-4	1.0279	1.0261	99.83	0.17	1.002
233-5	1.0368	1.0361	99.93	0.07	1.001
		average	**99.95**	**0.05**	**1.001**
		confidence limit	**0.15**	**0.15**	**0.001**
		SD	**0.12**	**0.12**	**0.001**
		RSD %	**0.12**	**217.28**	**0.119**

Method 9

JRC code	sample mass g	residue mass g	PAC %	soluble %	d
233-1	1.0538	1.0544	100.06	-0.06	0.999
233-2	1.0664	1.0641	99.79	0.21	1.002
233-3	1.0342	1.0339	99.97	0.03	1.000
233-4	1.0666	1.0672	100.06	-0.06	0.999
233-5	1.0260	1.0230	99.71	0.29	1.003
		average	**99.92**	**0.08**	**1.001**
		confidence limit	**0.20**	**0.20**	**0.002**
		SD	**0.16**	**0.16**	**0.002**
		RSD %	**0.16**	**189.57**	**0.161**

Method 10

JRC code	sample mass g	residue mass g	PAC %	soluble %	d
233-1	1.0246	1.0262	100.15	-0.15	0.998
233-2	1.0005	1.0040	100.35	-0.35	0.997
233-3	1.0095	1.0076	99.81	0.19	1.002
233-4	1.0055	1.0087	100.32	-0.32	0.997
233-5	0.9974	0.9998	100.24	-0.24	0.998
		average	**100.17**	**-0.17**	**0.998**
		confidence limit	**0.27**	**0.27**	**0.003**
		SD	**0.21**	**0.21**	**0.002**
		RSD %	**0.21**	**-123.54**	**0.217**

Method 11

JRC code	sample mass g	residue mass g	PAC %	soluble %	d
233-1	1.0177	1.0135	99.59	0.41	1.004
233-2	1.0287	1.0244	99.59	0.41	1.004
233-3	1.0248	1.0199	99.53	0.47	1.005
233-4	1.0169	1.0129	99.61	0.39	1.004
233-5	1.0247	1.0212	99.66	0.34	1.003
		average	**99.60**	**0.40**	**1.004**
		confidence limit	**0.06**	**0.06**	**0.001**
		SD	**0.05**	**0.05**	**0.0005**
		RSD %	**0.05**	**12.03**	**0.049**

Method 14

JRC code	sample mass g	residue mass g	PAC %	soluble %	d
233-1	1.0124	1.0056	99.33	0.67	1.007
233-2	1.0421	1.0357	99.39	0.61	1.006
233-3	1.0267	1.0204	99.39	0.61	1.006
233-4	1.0281	1.0227	99.48	0.52	1.005
233-5	1.0449	1.0387	99.41	0.59	1.006
		average	**99.40**	**0.60**	**1.006**
		confidence limit	**0.06**	**0.06**	**0.001**
		SD	**0.05**	**0.05**	**0.001**
		RSD %	**0.05**	**8.72**	**0.053**

Method 16

JRC code	sample mass g	residue mass g	insoluble %	soluble %
233-1	1.0752	0.8779	81.18	18.82
233-2	1.0141	0.8303	81.41	18.59
233-3	1.0056	0.8201	81.08	18.92
233-4	1.0411	0.8494	81.12	18.88
233-5	0.9986	0.8143	81.07	18.93
		average	**81.17**	**18.83**
		confidence limit	**0.17**	**0.17**
		SD	**0.14**	**0.14**
		RSD %	**0.17**	**0.74**

- ***Ventilated oven***

Method 1

JRC code	sample mass g	residue mass g	PAC %	soluble %	d
233-1	0.9855	0.9814	99.59	0.41	1.004
233-2	1.1205	1.1179	99.77	0.23	1.002
233-3	1.1177	1.1136	99.64	0.36	1.004
233-4	1.1427	1.1408	99.84	0.16	1.002
233-5	1.1537	1.1494	99.63	0.37	1.004
		average	**99.69**	**0.31**	**1.003**
		confidence limit	**0.13**	**0.13**	**0.001**
		SD	**0.11**	**0.11**	**0.001**
		RSD %	**0.11**	**34.18**	**0.107**

Method 2

JRC code	sample mass g	residue mass g	PAC %	soluble %	d
233-1	1.0231	1.0221	99.90	0.10	1.001
233-2	1.0174	1.0155	99.82	0.18	1.002
233-3	1.0134	1.0115	99.81	0.19	1.002
233-4	1.0391	1.0352	99.63	0.37	1.004
		average	**99.79**	**0.21**	**1.002**
		confidence limit	**0.18**	**0.18**	**0.002**
		SD	**0.12**	**0.12**	**0.001**
		RSD %	**0.12**	**55.17**	**0.117**

Method 5

JRC code	sample mass g	residue mass g	PAC %	soluble %	d
233-1	1.0977	1.0982	100.05	-0.05	1.000
233-2	1.0908	1.1096	101.71	-1.71	0.983
233-3	1.0718	1.0790	100.67	-0.67	0.993
233-4	1.0051	1.0166	101.13	-1.13	0.989
233-5	1.1545	1.1603	100.50	-0.50	0.995
		average	**100.81**	**-0.81**	**0.992**
		confidence limit	**0.79**	**0.79**	**0.008**
		SD	**0.63**	**0.63**	**0.006**
		RSD %	**0.63**	**-78.42**	**0.635**

Method 6

JRC code	sample mass g	residue mass g	PAC %	soluble %	d
233-1	1.0407	1.0380	99.74	0.26	1.003
233-2	1.0684	1.0653	99.71	0.29	1.003
233-3	1.0750	1.0722	99.74	0.26	1.003
233-4	1.0235	1.0211	99.77	0.23	1.002
233-5	1.0329	1.0299	99.71	0.29	1.003
		average	**99.74**	**0.26**	**1.003**
		confidence limit	**0.03**	**0.03**	**0.0003**
		SD	**0.02**	**0.02**	**0.0002**
		RSD %	**0.02**	**8.87**	**0.024**

Method 8

JRC code	sample mass g	residue mass g	PAC %	soluble %	d
233-1	1.0417	1.0417	100.00	0.00	1.000
233-2	1.0295	1.0301	100.06	-0.06	0.999
233-3	1.0374	1.0372	99.98	0.02	1.000
233-4	1.0215	1.0195	99.81	0.19	1.002
233-5	1.0261	1.0247	99.86	0.14	1.001
		average	**99.94**	**0.06**	**1.001**
		confidence limit	**0.13**	**0.13**	**0.001**
		SD	**0.10**	**0.10**	**0.001**
		RSD %	**0.10**	**177.86**	**0.104**

Method 9

JRC code	sample mass g	residue mass g	PAC %	soluble %	d
233-1	1.0489	1.0459	99.72	0.28	1.003
233-2	1.0331	1.0302	99.72	0.28	1.003
233-3	1.0461	1.0433	99.73	0.27	1.003
233-4	1.0602	1.0574	99.74	0.26	1.003
233-5	1.0460	1.0432	99.73	0.27	1.003
		average	**99.73**	**0.27**	**1.003**
		confidence limit	**0.01**	**0.01**	**0.0001**
		SD	**0.01**	**0.01**	**0.0001**
		RSD %	**0.01**	**3.49**	**0.010**

Method 10

JRC code	sample mass g	residue mass g	PAC %	soluble %	d
233-1	1.0136	1.0126	99.90	0.10	1.001
233-2	1.0082	1.0066	99.84	0.16	1.002
233-3	1.0139	1.0117	99.79	0.21	1.002
233-4	0.9950	0.9925	99.75	0.25	1.003
233-5	0.9436	0.9455	100.20	-0.20	0.998
		average	**99.90**	**0.10**	**1.001**
		confidence limit	**0.22**	**0.22**	**0.002**
		SD	**0.18**	**0.18**	**0.002**
		RSD %	**0.18**	**172.40**	**0.181**

Method 11

JRC code	sample mass g	residue mass g	PAC %	soluble %	d
233-1	1.0353	1.0304	99.53	0.47	1.005
233-2	1.026	1.021	99.52	0.48	1.005
233-3	1.0212	1.0164	99.53	0.47	1.005
233-4	1.0396	1.0344	99.50	0.50	1.005
233-5	1.0265	1.0223	99.59	0.41	1.004
		average	**99.54**	**0.46**	**1.005**
		confidence limit	**0.04**	**0.04**	**0.0004**
		SD	**0.03**	**0.03**	**0.0004**
		RSD %	**0.03**	**7.48**	**0.035**

Method 14

JRC code	sample mass g	residue mass g	PAC %	soluble %	d
233-1	1.0502	1.045	99.51	0.49	1.005
233-2	1.0181	1.0118	99.39	0.61	1.006
233-3	1.0571	1.0505	99.38	0.62	1.006
233-4	1.0225	1.0214	99.89	0.11	1.001
233-5	1.0542	1.0431	98.96	1.04	1.011
		average	**99.43**	**0.57**	**1.006**
		confidence limit	**0.42**	**0.42**	**0.004**
		SD	**0.33**	**0.33**	**0.003**
		RSD %	**0.34**	**58.34**	**0.340**

Method 16

JRC code	sample mass g	residue mass g	insoluble %	soluble %
233-1	0.9822	0.8014	81.12	18.88
233-2	1.0237	0.8352	81.12	18.88
233-3	1.0526	0.8590	81.14	18.86
233-4	1.0445	0.8522	81.12	18.88
233-5	1.0273	0.8382	81.12	18.88
		average	**81.12**	**18.88**
		confidence limit	**0.01**	**0.01**
		SD	**0.01**	**0.01**
		RSD %	**0.01**	**0.04**

PAC 40 % (sample 199)

- ***Vacuum oven***

Method 4

JRC code	sample mass g	residue mass g	insoluble %	soluble %
199-1	1.0790	0.7298	66.95	33.05
199-2	1.0825	0.7293	66.69	33.31
199-3	1.0691	0.7191	66.57	33.43
199-4	1.0637	0.7158	66.61	33.39
199-5	1.0511	0.7103	66.89	33.11
199-6	1.0244	0.6944	67.10	32.90
199-7	1.0361	0.7049	67.35	32.65
199-8	0.9972	0.6781	67.32	32.68
199-9	1.0566	0.7131	66.80	33.20
199-10	1.0779	0.7313	67.16	32.84
199-11	1.0283	0.6968	67.08	32.92
199-12	1.2898	0.8762	67.25	32.75
199-13	1.1020	0.7438	66.81	33.19
199-14	1.1711	0.7947	67.18	32.82
		average	**66.98**	**33.02**
		confidence limit	**0.19**	**0.19**
		SD	**0.26**	**0.26**
		RSD %	**0.39**	**0.79**

Method 7

JRC code	sample mass g	residue mass g	insoluble %	soluble %
199-1	1.0279	0.7145	68.85	31.15
199-2	1.0370	0.7144	68.22	31.78
199-3	1.0268	0.7108	68.56	31.44
199-4	1.0722	0.7369	68.06	31.94
199-5	1.0474	0.7247	68.52	31.48
199-6	1.0465	0.7287	68.97	31.03
199-7	1.0648	0.7372	68.57	31.43
199-8	1.0529	0.7305	68.72	31.28
199-9	1.0645	0.7400	68.85	31.15
199-10	1.0592	0.7311	68.36	31.64
		average	**68.57**	**31.43**
		confidence limit	**0.21**	**0.21**
		SD	**0.29**	**0.29**
		RSD %	**0.43**	**0.93**

Method 10

JRC code	sample mass g	residue mass g	PAC %	soluble %	d
199-1	1.0133	1.0133	100.00	0.00	1.000
199-2	1.0062	1.0057	99.95	0.05	1.000
199-3	1.0256	1.0248	99.92	0.08	1.001
199-4	1.0121	1.0101	99.81	0.19	1.002
199-5	1.0208	1.0194	99.87	0.13	1.001
199-6	1.0301	1.0294	99.93	0.07	1.001
199-7	0.9998	0.9988	99.90	0.10	1.001
199-8	1.0110	1.0099	99.89	0.11	1.001
199-9	1.0040	1.0024	99.84	0.16	1.002
199-10	1.0062	1.0057	99.95	0.05	1.000
		average	**99.91**	**0.09**	**1.001**
		confidence limit	**0.04**	**0.04**	**0.0004**
		SD	**0.06**	**0.06**	**0.001**
		RSD %	**0.06**	**61.71**	**0.059**

Method 11

JRC code	sample mass g	residue mass g	PAC %	soluble %	d
199-1	1.0624	1.0387	97.81	2.19	1.023
199-2	1.1102	1.0863	97.89	2.11	1.022
199-3	1.0455	1.0228	97.87	2.13	1.022
199-4	1.1353	1.1099	97.81	2.19	1.023
199-5	1.0223	0.9992	97.78	2.22	1.023
199-6	0.9119	0.8917	97.83	2.17	1.023
199-7	0.8517	0.8325	97.79	2.21	1.023
199-8	0.9301	0.9096	97.84	2.16	1.023
199-9	1.0053	0.984	97.92	2.08	1.022
		average	**97.84**	**2.16**	**1.0225**
		confidence limit	**0.04**	**0.04**	**0.0004**
		SD	**0.05**	**0.05**	**0.001**
		RSD %	**0.05**	**2.18**	**0.049**

Method 16

JRC code	sample mass g	residue mass g	insoluble %	soluble %
199-1	1.1414	0.7490	64.92	35.08
199-2	1.1199	0.7375	65.15	34.85
199-3	1.1946	0.7832	64.86	35.14
199-4	1.2122	0.7867	64.19	35.81
199-5	1.1229	0.7319	64.47	35.53
199-6	1.1241	0.7385	64.99	35.01
199-7	1.1334	0.7461	65.13	34.87
199-8	1.2088	0.7974	65.27	34.73
199-9	1.0901	0.7154	64.92	35.08
199-10	1.1170	0.7346	65.06	34.94
199-11	1.1259	0.7386	64.90	35.10
199-12	1.1094	0.7278	64.90	35.10
199-13	1.1338	0.7420	64.74	35.26
199-14	1.0351	0.6782	64.82	35.18
199-15	1.1628	0.7624	64.86	35.14
199-16	1.0895	0.7128	64.72	35.28
199-17	1.1087	0.7264	64.81	35.19
199-18	1.0774	0.7063	64.85	35.15
199-19	1.1229	0.7349	64.74	35.26
199-20	1.1552	0.7505	64.26	35.74
199-21	1.0829	0.7098	64.84	35.16
199-22	1.0483	0.6867	64.80	35.20
199-23	1.0191	0.6674	64.78	35.22
199-24	1.0405	0.6815	64.79	35.21
199-25	1.0162	0.6659	64.82	35.18
		average	**64.82**	**35.18**
		confidence limit	**0.10**	**0.10**
		SD	**0.24**	**0.24**
		RSD %	**0.37**	**0.68**

• *Ventilated oven*

Method 4

JRC code	sample mass g	residue mass g	insoluble %	soluble %
199-1	1.1143	0.7551	67.08	32.92
199-2	1.0235	0.6920	66.93	33.07
199-3	1.0126	0.6857	67.03	32.97
199-4	1.0331	0.6991	66.99	33.01
199-5	1.0453	0.7065	66.90	33.10
199-6	1.0468	0.7051	66.67	33.33
199-7	1.0102	0.6821	66.84	33.16
199-8	0.9950	0.6704	66.69	33.31
199-9	1.0236	0.6883	66.56	33.44
199-10	1.0464	0.7039	66.58	33.42
		average	**66.83**	**33.17**
		confidence limit	**0.14**	**0.14**
		SD	**0.19**	**0.19**
		RSD %	**0.29**	**0.57**

Method 7

JRC code	sample mass g	residue mass g	insoluble %	soluble %
199-1	1.0121	0.6939	67.89	32.11
199-2	1.0216	0.7028	68.12	31.88
199-3	1.0421	0.7202	68.44	31.56
199-4	1.0316	0.7122	68.37	31.63
199-5	1.0093	0.6952	68.21	31.79
199-6	1.0117	0.7009	68.61	31.39
199-7	1.0612	0.7367	68.76	31.24
199-8	1.0577	0.7362	68.94	31.06
199-9	0.9897	0.6888	68.94	31.06
199-10	0.9481	0.6577	68.71	31.29
		average	**68.50**	**31.50**
		confidence limit	**0.25**	**0.25**
		SD	**0.35**	**0.35**
		RSD %	**0.52**	**1.12**

Method 10

JRC code	sample mass g	residue mass g	PAC %	soluble %	d
199-1	1.0764	1.0754	99.91	0.09	1.001
199-2	1.0577	1.0565	99.89	0.11	1.001
199-3	1.0591	1.0561	99.72	0.28	1.003
199-4	1.0345	1.0334	99.90	0.10	1.001
		average	**99.85**	**0.15**	**1.001**
		confidence limit	**0.14**	**0.14**	**0.001**
		SD	**0.09**	**0.09**	**0.001**
		RSD %	**0.09**	**60.36**	**0.090**

Method 11

JRC code	sample mass	residue mass	PAC	soluble	d
	g	g	%	%	
199-1	1.0049	0.9744	97.02	2.98	1.031
199-2	1.0328	1.0013	97.01	2.99	1.031
199-3	1.0367	1.0054	97.04	2.96	1.031
199-4	1.0196	0.9883	96.99	3.01	1.032
199-5	1.0117	0.9815	97.07	2.93	1.031
199-6	0.9934	0.9632	97.02	2.98	1.031
199-7	0.9973	0.9675	97.07	2.93	1.031
199-8	1.0178	0.9834	96.68	3.32	1.035
199-9	1.0084	0.9775	96.99	3.01	1.032
199-10	1.0106	0.9764	96.68	3.32	1.035
		average	**96.96**	**3.04**	**1.032**
		confidence limit	**0.11**	**0.11**	**0.001**
		SD	**0.15**	**0.15**	**0.002**
		RSD %	**0.15**	**4.85**	**0.156**

Method 16

JRC code	sample mass	residue mass	insoluble	soluble
	g	g	%	%
199-1	1.0794	0.7070	64.79	35.21
199-2	1.0589	0.6935	64.79	35.21
199-3	1.0091	0.6613	64.83	35.17
199-4	1.0220	0.6690	64.75	35.25
199-5	1.0428	0.6831	64.80	35.20
199-6	1.0067	0.6579	64.65	35.35
199-7	1.0126	0.6637	64.84	35.16
199-8	1.0584	0.6923	64.70	35.30
199-9	1.0106	0.6602	64.62	35.38
199-10	1.0541	0.6888	64.64	35.36
		average	**64.74**	**35.26**
		confidence limit	**0.06**	**0.06**
		SD	**0.08**	**0.08**
		RSD %	**0.13**	**0.23**

Solubility properties – *d* correction factors

polypropylene (samples 113, 186, 187, 192)

Method 1

JRC code	sample mass g	residue mass g	PP %	soluble %	d
186-1	1.1102	1.1090	99.90	0.10	1.001
186-2	1.0691	1.0662	99.74	0.26	1.003
186-3	1.0303	1.0270	99.69	0.31	1.003
186-4	0.9821	0.9794	99.73	0.27	1.003
186-5	0.9299	0.9282	99.82	0.18	1.002
187-6	1.0078	1.0048	99.71	0.29	1.003
187-7	0.9851	0.9845	99.94	0.06	1.001
187-8	1.0045	1.0020	99.76	0.24	1.002
187-9	1.0004	0.9993	99.89	0.11	1.001
187-10	0.8950	0.8920	99.67	0.33	1.003
192-11	1.0453	1.0418	99.67	0.33	1.003
192-12	1.0399	1.0367	99.70	0.30	1.003
192-13	1.0798	1.0759	99.65	0.35	1.004
192-14	1.0669	1.0639	99.73	0.27	1.003
192-15	1.0155	1.0122	99.68	0.32	1.003
192-16	1.0519	1.0491	99.74	0.26	1.003
192-17	1.0335	1.0308	99.75	0.25	1.003
192-18	1.0395	1.0364	99.71	0.29	1.003
192-19	1.0387	1.0363	99.78	0.22	1.002
192-20	1.0174	1.0148	99.75	0.25	1.003
		average	**99.75**	**0.25**	**1.003**
		confidence limit	**0.04**	**0.04**	**0.0004**
		SD	**0.08**	**0.08**	**0.001**
		RSD %	**0.08**	**31.90**	**0.082**

Method 3

JRC code	sample mass g	residue mass g	PP %	soluble %	d
192-1	1.1342	1.1323	99.84	0.16	1.002
192-2	1.1944	1.1940	99.97	0.03	1.000
192-3	1.0948	1.0943	99.96	0.04	1.000
192-4	1.0051	1.0054	100.03	-0.03	1.000
192-5	1.1128	1.1108	99.83	0.17	1.002
192-6	1.0070	1.0045	99.76	0.24	1.002
192-7	0.9898	0.9867	99.70	0.30	1.003
192-8	0.9961	0.9956	99.95	0.05	1.001
192-9	1.0016	1.0007	99.91	0.09	1.001
192-10	0.9904	0.9898	99.94	0.06	1.001
192-11	1.0626	1.0610	99.85	0.15	1.002
192-12	1.0352	1.0339	99.88	0.12	1.001
192-13	1.0240	1.0217	99.78	0.22	1.002
192-14	1.0284	1.0264	99.81	0.19	1.002
192-15	1.0156	1.0143	99.88	0.12	1.001
192-16	1.0202	1.0202	100.00	0.00	1.000
192-17	1.0108	1.0110	100.02	-0.02	1.000
192-18	1.0201	1.0202	100.01	-0.01	1.000
192-19	1.0217	1.0203	99.87	0.13	1.001
192-20	1.0206	1.0202	99.96	0.04	1.000
		average	**99.90**	**0.10**	**1.001**
		confidence limit	**0.04**	**0.04**	**0.0005**
		SD	**0.09**	**0.09**	**0.001**
		RSD %	**0.09**	**90.39**	**0.096**

Method 5

JRC code	sample mass	residue mass	PP	soluble	d
	g	g	%	%	
192-1	1.0812	1.0812	100.00	0.00	1.000
192-2	1.1810	1.1789	99.83	0.17	1.002
192-3	1.0343	1.0347	100.04	-0.04	1.000
192-4	0.9650	0.9648	99.98	0.02	1.000
192-5	1.0002	0.9997	99.95	0.05	1.001
192-6	0.9717	0.9715	99.98	0.02	1.000
192-7	0.9829	0.9811	99.82	0.18	1.002
192-8	1.0049	1.0045	99.96	0.04	1.000
192-9	0.9911	0.9914	100.03	-0.03	1.000
192-10	1.0146	1.0128	99.83	0.17	1.002
192-11	1.0227	1.0206	99.80	0.20	1.002
192-12	1.0175	1.0155	99.81	0.19	1.002
192-13	1.0216	1.0194	99.79	0.21	1.002
192-14	1.0262	1.0238	99.77	0.23	1.002
192-15	1.0154	1.0132	99.79	0.21	1.002
192-16	1.0187	1.0164	99.78	0.22	1.002
192-17	1.0362	1.0340	99.79	0.21	1.002
192-18	1.0474	1.0449	99.77	0.23	1.002
192-19	1.0375	1.0356	99.82	0.18	1.002
		average	**99.87**	**0.13**	**1.001**
		confidence limit	**0.05**	**0.05**	**0.0005**
		SD	**0.10**	**0.10**	**0.001**
		RSD %	**0.10**	**75.76**	**0.101**

Method 6

JRC code	sample mass	residue mass	PP	soluble	d
	g	g	%	%	
186-1	0.9458	0.9417	99.58	0.42	1.004
186-2	1.1322	1.1291	99.73	0.27	1.003
186-3	1.2013	1.1974	99.68	0.32	1.003
186-4	1.1845	1.1799	99.62	0.38	1.004
186-5	1.0465	1.0424	99.62	0.38	1.004
187-6	0.9995	0.9968	99.74	0.26	1.003
187-7	1.0007	0.9980	99.74	0.26	1.003
187-8	0.9978	0.9943	99.66	0.34	1.004
187-9	0.9969	0.9926	99.58	0.42	1.004
187-10	1.0168	1.0140	99.73	0.27	1.003
192-11	1.0474	1.0458	99.85	0.15	1.002
192-12	1.0616	1.0595	99.81	0.19	1.002
192-13	1.0318	1.0318	100.00	0.00	1.000
192-14	1.0394	1.0393	99.99	0.01	1.000
192-15	1.0247	1.0238	99.91	0.09	1.001
192-16	1.0393	1.0391	99.98	0.02	1.000
192-17	1.0319	1.0304	99.86	0.14	1.001
192-18	1.0128	1.0113	99.86	0.14	1.001
192-19	1.0509	1.0491	99.83	0.17	1.002
192-20	1.0645	1.0630	99.86	0.14	1.001
		average	**99.78**	**0.22**	**1.002**
		confidence limit	**0.06**	**0.06**	**0.001**
		SD	**0.13**	**0.13**	**0.001**
		RSD %	**0.13**	**61.55**	**0.138**

Method 7

JRC code	sample mass g	residue mass g	PP %	soluble %	d
192-1	0.5410	0.5404	99.89	0.11	1.001
192-2	0.9873	0.9855	99.82	0.18	1.002
192-3	0.7601	0.7598	99.96	0.04	1.000
192-4	1.0655	1.0634	99.81	0.19	1.002
192-5	1.1154	1.1142	99.90	0.10	1.001
192-6	1.0072	1.0051	99.80	0.20	1.002
192-7	0.9940	0.9932	99.92	0.08	1.001
192-8	0.9879	0.9856	99.77	0.23	1.002
192-9	0.9391	0.9377	99.86	0.14	1.001
192-10	1.0139	1.0140	100.01	-0.01	1.000
192-11	1.0274	1.0324	100.47	-0.47	0.995
192-12	1.0218	1.0268	100.48	-0.48	0.995
192-13	1.0174	1.0223	100.47	-0.47	0.995
192-14	1.0325	1.0359	100.32	-0.32	0.997
192-15	1.0160	1.0202	100.40	-0.40	0.996
192-16	1.0660	1.0702	100.38	-0.38	0.996
192-17	1.0316	1.0424	101.02	-1.02	0.990
192-18	1.0393	1.0502	101.02	-1.02	0.990
192-19	1.0207	1.0235	100.27	-0.27	0.997
192-20	1.0232	1.0268	100.34	-0.34	0.996
		average	**100.19**	**-0.19**	**0.998**
		confidence limit	**0.18**	**0.18**	**0.002**
		SD	**0.38**	**0.38**	**0.004**
		RSD %	**0.38**	**-196.31**	**0.392**

Method 8

JRC code	sample mass g	residue mass g	PP %	soluble %	d
192-1	1.2085	1.2078	99.94	0.06	1.001
192-2	1.2337	1.2335	99.98	0.02	1.000
192-3	1.0034	1.0013	99.80	0.20	1.002
192-4	1.1167	1.1167	100.00	0.00	1.000
192-5	1.2237	1.2202	99.72	0.28	1.003
192-6	1.0036	1.0034	99.98	0.02	1.000
192-7	1.0057	1.0054	99.97	0.03	1.000
192-8	1.0153	1.0149	99.96	0.04	1.000
192-9	1.0943	1.0938	99.96	0.04	1.000
192-10	1.0076	1.0063	99.87	0.13	1.001
192-11	0.9651	0.9642	99.91	0.09	1.001
192-12	1.0419	1.0399	99.81	0.19	1.002
192-13	0.9167	0.9161	99.94	0.06	1.001
192-14	1.0354	1.0343	99.90	0.10	1.001
192-15	1.0288	1.0275	99.88	0.12	1.001
192-16	1.0355	1.0350	99.95	0.05	1.000
192-17	1.0349	1.0339	99.91	0.09	1.001
192-18	1.0452	1.0441	99.90	0.10	1.001
192-19	1.0313	1.0308	99.95	0.05	1.000
192-20	1.0200	1.0201	100.01	-0.01	1.000
		average	**99.92**	**0.08**	**1.001**
		confidence limit	**0.03**	**0.03**	**0.0004**
		SD	**0.07**	**0.07**	**0.001**
		RSD %	**0.07**	**88.28**	**0.075**

Method 9

JRC code	sample mass g	residue mass g	PP %	soluble %	d
192-1	0.9498	0.9447	99.48	0.52	1.005
192-2	0.9508	0.9470	99.61	0.39	1.004
192-3	1.4469	1.4395	99.50	0.50	1.005
192-4	1.1444	1.1386	99.51	0.49	1.005
192-5	1.0148	1.0101	99.55	0.45	1.005
192-6	0.9806	0.9757	99.51	0.49	1.005
192-7	1.0018	0.9980	99.63	0.37	1.004
192-8	0.9704	0.9674	99.70	0.30	1.003
192-9	1.0178	1.0140	99.64	0.36	1.004
192-10	1.0104	1.0063	99.61	0.39	1.004
192-11	1.0448	1.0421	99.75	0.25	1.003
192-12	1.0005	0.9995	99.90	0.10	1.001
192-13	1.0231	1.0218	99.88	0.12	1.001
192-14	1.0223	1.0171	99.50	0.50	1.005
192-15	1.0167	1.0114	99.49	0.51	1.005
192-16	1.0121	1.0104	99.84	0.16	1.002
192-17	1.0163	1.0143	99.81	0.19	1.002
192-18	1.0335	1.0285	99.53	0.47	1.005
192-19	1.0165	1.0152	99.87	0.13	1.001
192-20	1.0229	1.0178	99.51	0.49	1.005
		average	**99.64**	**0.36**	**1.004**
		confidence limit	**0.07**	**0.07**	**0.0007**
		SD	**0.15**	**0.15**	**0.002**
		RSD %	**0.15**	**41.35**	**0.153**

Method 10

JRC code	sample mass g	residue mass g	PP %	soluble %	d
192-1	0.9304	0.9292	99.87	0.13	1.001
192-2	1.1085	1.1053	99.72	0.28	1.003
192-3	0.9109	0.9106	99.97	0.03	1.000
192-4	1.1011	1.0980	99.73	0.27	1.003
192-5	1.0792	1.0762	99.73	0.27	1.003
192-6	0.9956	0.9931	99.76	0.24	1.003
192-7	0.9773	0.9740	99.67	0.33	1.003
192-8	1.0152	1.0125	99.74	0.26	1.003
192-9	0.9971	0.9947	99.77	0.23	1.002
192-10	0.9911	0.9880	99.70	0.30	1.003
192-11	1.0408	1.0401	99.93	0.07	1.001
192-12	1.0337	1.0329	99.92	0.08	1.001
192-13	1.0228	1.0222	99.94	0.06	1.001
192-14	1.0188	1.0184	99.96	0.04	1.000
192-15	1.0213	1.0204	99.91	0.09	1.001
192-16	1.0314	1.0305	99.92	0.08	1.001
192-17	1.0401	1.0398	99.97	0.03	1.000
192-18	1.0553	1.0552	99.99	0.01	1.000
192-19	1.0519	1.0518	99.99	0.01	1.000
192-20	1.0175	1.0174	99.99	0.01	1.000
		average	**99.86**	**0.14**	**1.001**
		confidence limit	**0.05**	**0.05**	**0.001**
		SD	**0.12**	**0.12**	**0.001**
		RSD %	**0.12**	**83.06**	**0.120**

Method 11

JRC code	sample mass g	residue mass g	PP %	soluble %	d
192-1	1.0715	1.0717	100.02	-0.02	1.000
192-2	0.5793	0.5789	99.93	0.07	1.001
192-3	1.0011	1.0010	99.99	0.01	1.000
192-4	1.1259	1.1263	100.03	-0.03	1.000
192-5	1.0961	1.0955	99.95	0.05	1.001
192-6	1.0055	1.0058	100.03	-0.03	1.000
192-7	1.0060	1.0048	99.88	0.12	1.001
192-8	1.0010	1.0002	99.92	0.08	1.001
192-9	1.0017	1.0020	100.03	-0.03	1.000
192-10	0.9900	0.9868	99.69	0.31	1.003
192-11	1.0545	1.0597	100.48	-0.48	0.995
192-12	1.0745	1.0762	100.15	-0.15	0.998
192-13	1.0194	1.0198	100.04	-0.04	1.000
192-14	1.0296	1.0320	100.23	-0.23	0.998
192-15	1.0171	1.0134	99.65	0.35	1.004
192-16	1.0184	1.0200	100.15	-0.15	0.998
192-17	1.0226	1.0192	99.68	0.32	1.003
192-18	1.0393	1.0410	100.16	-0.16	0.998
192-19	1.0107	1.0127	100.19	-0.19	0.998
192-20	1.0112	1.0117	100.05	-0.05	1.000
		average	**100.01**	**-0.01**	**1.000**
		confidence limit	**0.09**	**0.09**	**0.001**
		SD	**0.20**	**0.20**	**0.002**
		RSD %	**0.20**	**-1615.43**	**0.204**

Method 14

JRC code	sample mass g	residue mass g	PP %	soluble %	d
192-1	0.5685	0.5683	99.97	0.03	1.000
192-2	0.7926	0.7926	100.00	0.00	1.000
192-3	0.8798	0.8784	99.85	0.15	1.002
192-4	0.9709	0.9701	99.92	0.08	1.001
192-5	0.6646	0.6633	99.81	0.19	1.002
192-6	0.9940	0.9940	100.00	0.00	1.000
192-7	1.0270	1.0262	99.92	0.08	1.001
192-8	0.9357	0.9339	99.81	0.19	1.002
192-9	1.0070	1.0041	99.72	0.28	1.003
192-10	1.0086	1.0070	99.85	0.15	1.002
192-11	1.0237	1.0290	100.50	-0.50	0.995
192-12	1.0444	1.0435	99.92	0.08	1.001
192-13	1.0367	1.0378	100.10	-0.10	0.999
192-14	1.0210	1.0209	99.99	0.01	1.000
192-15	1.0152	1.0209	100.55	-0.55	0.994
192-16	1.0223	1.0210	99.88	0.12	1.001
192-17	1.0119	1.0112	99.93	0.07	1.001
192-18	1.0121	1.0166	100.43	-0.43	0.996
		average	**100.01**	**-0.01**	**1.000**
		confidence limit	**0.12**	**0.12**	**0.001**
		SD	**0.24**	**0.24**	**0.002**
		RSD %	**0.24**	**-3008.91**	**0.247**

Method 15

JRC code	sample mass g	residue mass g	soluble %	PP %
113-1	0.2238	0.0001	0.04	99.96
113-2	0.5726	-0.0006	-0.10	100.10
113-3	0.3984	0.0001	0.02	99.98
113-4	0.3729	-0.0001	-0.03	100.03
113-5	0.3674	0.0001	0.03	99.97
113-6	0.4007	0.0002	0.05	99.95
113-7	0.3701	-0.0001	-0.03	100.03
113-8	0.4483	0.0001	0.02	99.98
113-9	0.5311	0.0001	0.02	99.98
113-10	0.4600	0.0001	0.02	99.98
		average	0.005	100.00
		confidence limit	0.03	0.03
		SD	0.05	0.05
		RSD %	906.12	0.05

Method 16

JRC code	sample mass g	residue mass g	PP %	soluble %	d
192-1	1.1827	1.1805	99.82	0.18	1.002
192-2	0.9492	0.9474	99.82	0.18	1.002
192-3	1.2121	1.2091	99.76	0.24	1.002
192-4	1.0966	1.0948	99.84	0.16	1.002
192-5	1.0006	0.9967	99.62	0.38	1.004
192-6	1.0300	1.0256	99.59	0.41	1.004
192-7	1.0236	1.0209	99.74	0.26	1.003
192-8	0.9808	0.9768	99.60	0.40	1.004
192-9	0.8770	0.8750	99.78	0.22	1.002
192-10	1.0349	1.0335	99.87	0.13	1.001
192-11	1.0480	1.0459	99.81	0.19	1.002
192-12	1.0377	1.0356	99.80	0.20	1.002
192-13	1.0240	1.0219	99.80	0.20	1.002
192-14	1.0299	1.0277	99.79	0.21	1.002
192-15	1.0130	1.0110	99.81	0.19	1.002
192-16	1.0480	1.0459	99.81	0.19	1.002
192-17	1.0377	1.0356	99.80	0.20	1.002
192-18	1.0240	1.0219	99.80	0.20	1.002
192-19	1.0299	1.0277	99.79	0.21	1.002
192-20	1.0130	1.0110	99.81	0.19	1.002
		average	99.77	0.23	1.002
		confidence limit	0.04	0.04	0.0004
		SD	0.08	0.08	0.001
		RSD %	0.08	34.16	0.080

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Method 3

JRC code	sample mass g	residue mass g	insoluble %	PA6 %
193-1	0.9703	0.0017	0.17	99.83
193-2	0.9893	0.0023	0.22	99.78
193-3	1.1739	0.0012	0.10	99.90
193-4	1.0699	0.0008	0.07	99.93
193-5	0.9709	0.0016	0.16	99.84
193-6	0.9620	0.0018	0.18	99.82
193-7	1.0019	0.0009	0.08	99.92
193-8	1.0050	0.0008	0.08	99.92
193-9	1.0009	0.0011	0.10	99.90
193-10	1.0106	0.0007	0.07	99.93
		average	0.12	99.88
		confidence limit	0.04	0.04
		SD	0.05	0.05
		RSD %	44.22	0.05

Method 5

JRC code	sample mass g	residue mass g	PA6 %	soluble %	d
193-1	1.0711	1.0688	99.80	0.20	1.002
193-2	1.0147	1.0103	99.59	0.41	1.004
193-3	1.0359	1.0350	99.92	0.08	1.001
193-4	0.9992	0.9970	99.79	0.21	1.002
193-5	1.1574	1.1542	99.74	0.26	1.003
193-6	1.0069	1.0057	99.89	0.11	1.001
193-7	0.9622	0.9589	99.68	0.32	1.003
193-8	1.0011	0.9988	99.78	0.22	1.002
193-9	1.0706	1.0673	99.71	0.29	1.003
193-10	0.9115	0.9086	99.70	0.30	1.003
		average	**99.76**	**0.24**	**1.003**
		confidence limit	**0.07**	**0.07**	**0.001**
		SD	**0.10**	**0.10**	**0.001**
		RSD %	**0.10**	**40.74**	**0.104**

Method 7

JRC code	sample mass g	residue mass g	insoluble %	PA6 %
193-1	0.9684	0.0026	0.25	99.75
193-2	0.7825	0.0009	0.11	99.89
193-3	1.1117	0.0013	0.11	99.89
193-4	0.8248	0.0017	0.19	99.81
193-5	1.0367	0.0010	0.09	99.91
193-6	0.9920	0.0009	0.09	99.91
193-7	1.0065	0.0014	0.13	99.87
193-8	1.0060	0.0012	0.11	99.89
193-9	0.9866	0.0010	0.10	99.90
193-10	0.9903	0.0013	0.12	99.88
		average	**0.13**	**99.87**
		confidence limit	**0.04**	**0.04**
		SD	**0.05**	**0.05**
		RSD %	**40.52**	**0.05**

Method 10

JRC code	sample mass g	residue mass g	PA6 %	soluble %	d
193-1	0.9757	0.9632	98.79	1.21	1.013
193-2	1.0649	1.0522	98.87	1.13	1.012
193-3	0.9479	0.9368	98.89	1.11	1.012
193-4	0.9608	0.9496	98.90	1.10	1.012
193-5	0.8802	0.8710	99.01	0.99	1.011
193-6	1.0008	0.9888	98.87	1.13	1.012
193-7	0.9908	0.9793	98.90	1.10	1.012
193-8	1.0089	0.9976	98.94	1.06	1.011
193-9	0.9989	0.9870	98.87	1.13	1.012
193-10	0.9906	0.9810	99.08	0.92	1.010
		average	**98.91**	**1.09**	**1.012**
		confidence limit	**0.06**	**0.06**	**0.001**
		SD	**0.08**	**0.08**	**0.001**
		RSD %	**0.08**	**7.59**	**0.088**

Method 11

JRC code	sample mass	residue mass	insoluble	PA6
	g	g	%	%
193-1	1.0356	0.0012	0.11	99.89
193-2	1.0509	0.0011	0.10	99.90
193-3	1.0631	0.0012	0.11	99.89
193-4	1.0013	0.0014	0.13	99.87
193-5	0.9568	0.0015	0.15	99.85
193-6	0.9591	0.0010	0.10	99.90
193-7	0.9894	0.0015	0.14	99.86
193-8	1.0009	0.0016	0.15	99.85
193-9	0.9960	0.0013	0.12	99.88
193-10	1.0090	0.0012	0.11	99.89
		average	**0.12**	**99.88**
		confidence limit	**0.01**	**0.01**
		SD	**0.02**	**0.02**
		RSD %	**16.46**	**0.02**

Method 16

JRC code	sample mass	residue mass	insoluble	PA6
	g	g	%	%
193-1	1.0523	0.0010	0.09	99.91
193-2	0.8789	0.0005	0.05	99.95
193-3	0.9547	0.0002	0.02	99.98
193-4	1.0452	0.0010	0.09	99.91
193-5	1.1815	0.0010	0.08	99.92
193-6	1.0080	0.0011	0.10	99.90
193-7	0.9960	0.0006	0.06	99.94
193-8	1.0002	0.0006	0.06	99.94
193-9	0.9921	0.0007	0.07	99.93
193-10	1.0987	0.0012	0.10	99.90
		average	**0.07**	**99.93**
		confidence limit	**0.02**	**0.02**
		SD	**0.03**	**0.03**
		RSD %	**36.47**	**0.03**

PAC 5 % (sample 195)

- ## *Vacuum oven*

Method 11

JRC code	sample mass g	residue mass g	PAC %	soluble %	d
195-1	1.0029	1.0020	99.91	0.09	1.001
195-2	1.0256	1.0245	99.89	0.11	1.001
195-3	1.0047	1.0037	99.90	0.10	1.001
195-4	1.0480	1.0467	99.88	0.12	1.001
195-5	1.0173	1.0160	99.87	0.13	1.001
195-6	1.0233	1.0219	99.86	0.14	1.001
195-7	1.0821	1.0803	99.84	0.16	1.002
195-8	1.0189	1.0174	99.85	0.15	1.001
195-9	1.0268	1.0252	99.85	0.15	1.002
195-10	1.0218	1.0196	99.79	0.21	1.002
		average	**99.86**	**0.14**	**1.001**
		confidence limit	**0.03**	**0.03**	**0.0003**
		SD	**0.04**	**0.04**	**0.0004**
		RSD %	**0.04**	**26.91**	**0.037**

- ## *Ventilated oven*

Method 11

JRC code	sample mass g	residue mass g	PAC %	soluble %	d
195-1	1.0195	1.0200	100.05	-0.05	1.000
195-2	1.0330	1.0236	99.10	0.90	1.009
195-3	1.0273	1.0305	100.31	-0.31	0.997
195-4	1.0350	1.0258	99.12	0.88	1.009
195-5	1.0270	1.0301	100.30	-0.30	0.997
195-6	1.0229	1.0273	100.43	-0.43	0.996
195-7	1.0161	1.0210	100.48	-0.48	0.995
195-8	1.0267	1.0280	100.13	-0.13	0.999
195-9	1.0326	1.0325	99.99	0.01	1.000
195-10	1.0447	1.0403	99.58	0.42	1.004
		average	**99.95**	**0.05**	**1.001**
		confidence limit	**0.37**	**0.37**	**0.004**
		SD	**0.51**	**0.51**	**0.005**
		RSD %	**0.51**	**975.38**	**0.518**

PAC 10 % (sample 196)

- ## *Vacuum oven*

Method 11

JRC code	sample mass g	residue mass g	PAC %	soluble %	d
196-1	1.0083	1.0060	99.77	0.23	1.002
196-2	0.9985	0.9957	99.72	0.28	1.003
196-3	1.0367	1.0309	99.45	0.55	1.006
196-4	1.0233	1.0206	99.74	0.26	1.003
196-5	1.0632	1.0563	99.36	0.64	1.007
196-6	1.0408	1.0345	99.40	0.60	1.006
196-7	1.0649	1.0621	99.74	0.26	1.003
196-8	0.9993	0.9946	99.53	0.47	1.005
196-9	1.0355	1.0332	99.78	0.22	1.002
196-10	1.0222	1.0199	99.78	0.22	1.002
		average	**99.63**	**0.37**	**1.004**
		confidence limit	**0.12**	**0.12**	**0.001**
		SD	**0.17**	**0.17**	**0.002**
		RSD %	**0.17**	**46.20**	**0.175**

- ***Ventilated oven***

Method 11

JRC code	sample mass g	residue mass g	PAC %	soluble %	d
196-1	1.0522	1.0602	100.75	-0.75	0.992
196-2	1.0159	1.0134	99.76	0.24	1.002
196-3	1.0333	1.0275	99.44	0.56	1.006
196-4	1.0282	1.0373	100.88	-0.88	0.991
196-5	1.0218	1.0305	100.84	-0.84	0.992
196-6	1.0233	1.0267	100.33	-0.33	0.997
196-7	1.0026	1.0046	100.20	-0.20	0.998
196-8	1.0125	1.0174	100.48	-0.48	0.995
196-9	1.0294	1.0321	100.26	-0.26	0.997
196-10	1.0407	1.0452	100.43	-0.43	0.996
		average	**100.34**	**-0.34**	**0.997**
		confidence limit	**0.33**	**0.33**	**0.003**
		SD	**0.46**	**0.46**	**0.005**
		RSD %	**0.46**	**-136.79**	**0.465**

PAC 20 % (sample 197)

- ***Vacuum oven***

Method 11

JRC code	sample mass g	residue mass g	PAC %	soluble %	d
197-1	1.0188	1.0165	99.78	0.22	1.002
197-2	1.0253	1.0212	99.60	0.40	1.004
197-3	1.0192	1.0127	99.37	0.63	1.006
197-4	1.0232	1.0184	99.54	0.46	1.005
197-5	1.0278	1.0190	99.15	0.85	1.009
197-6	1.0357	1.0317	99.62	0.38	1.004
197-7	1.0362	1.0284	99.25	0.75	1.008
197-8	1.0039	0.9975	99.37	0.63	1.006
197-9	1.0224	1.0180	99.57	0.43	1.004
197-10	1.0221	1.0174	99.54	0.46	1.005
		average	**99.48**	**0.52**	**1.005**
		confidence limit	**0.14**	**0.14**	**0.001**
		SD	**0.19**	**0.19**	**0.002**
		RSD %	**0.19**	**36.31**	**0.192**

- ***Ventilated oven***

Method 11

JRC code	sample mass g	residue mass g	PAC %	soluble %	d
197-1	1.2283	1.2223	99.52	0.48	1.005
197-2	1.1943	1.1878	99.46	0.54	1.005
197-3	1.2165	1.2111	99.56	0.44	1.004
197-4	1.2368	1.2308	99.52	0.48	1.005
197-5	1.2010	1.1955	99.55	0.45	1.005
197-6	1.1912	1.1856	99.53	0.47	1.005
197-7	1.1829	1.1775	99.55	0.45	1.005
197-8	1.1951	1.1896	99.54	0.46	1.005
197-9	1.2018	1.1956	99.49	0.51	1.005
		average	**99.52**	**0.48**	**1.005**
		confidence limit	**0.02**	**0.02**	**0.0003**
		SD	**0.03**	**0.03**	**0.0003**
		RSD %	**0.03**	**6.73**	**0.032**

PAC 30 % (sample 198)

- ## *Vacuum oven*

Method 11

JRC code	sample mass g	residue mass g	PAC %	soluble %	d
198-1	1.0656	1.0541	98.93	1.07	1.011
198-2	1.0338	1.0229	98.96	1.04	1.011
198-3	0.9473	0.9387	99.10	0.90	1.009
198-4	1.0412	1.0310	99.03	0.97	1.010
198-5	1.2329	1.2202	98.98	1.02	1.010
198-6	1.0445	1.0351	99.11	0.89	1.009
198-7	0.9791	0.9695	99.03	0.97	1.010
198-8	0.9464	0.9379	99.11	0.89	1.009
198-9	0.9575	0.9478	99.00	1.00	1.010
198-10	0.9565	0.9478	99.10	0.90	1.009
		average	**99.03**	**0.97**	**1.010**
		confidence limit	**0.05**	**0.05**	**0.0005**
		SD	**0.07**	**0.07**	**0.001**
		RSD %	**0.07**	**7.01**	**0.069**

- ## *Ventilated oven*

Method 11

JRC code	sample mass g	residue mass g	PAC %	soluble %	d
198-1	1.0258	1.0182	99.27	0.73	1.007
198-2	1.0090	1.0002	99.14	0.86	1.009
198-3	1.0166	1.0088	99.24	0.76	1.008
198-4	1.0257	1.0179	99.25	0.75	1.008
198-5	1.0416	1.0320	99.09	0.91	1.009
198-6	1.0311	1.0248	99.40	0.60	1.006
198-7	1.0337	1.0274	99.40	0.60	1.006
198-8	1.0397	1.0327	99.33	0.67	1.007
198-9	1.0165	1.0080	99.17	0.83	1.008
198-10	1.0107	1.0050	99.44	0.56	1.006
		average	**99.27**	**0.73**	**1.007**
		confidence limit	**0.09**	**0.09**	**0.001**
		SD	**0.12**	**0.12**	**0.001**
		RSD %	**0.12**	**16.33**	**0.121**

PAC 40 % (sample 199)

- ## *Vacuum oven*

Method 1

JRC code	sample mass g	residue mass g	PAC %	soluble %	d
199-1	0.9697	0.9655	99.57	0.43	1.004
199-2	0.8080	0.8042	99.53	0.47	1.005
199-3	0.9684	0.9644	99.59	0.41	1.004
199-4	1.0545	1.0492	99.50	0.50	1.005
199-5	0.8873	0.8834	99.56	0.44	1.004
199-6	1.0198	1.0120	99.24	0.76	1.008
199-7	1.0593	1.0560	99.69	0.31	1.003
199-8	1.0056	1.0020	99.65	0.35	1.004
199-9	1.0741	1.0673	99.37	0.63	1.006
199-10	1.1646	1.1611	99.70	0.30	1.003
		average	**99.54**	**0.46**	**1.005**
		confidence limit	**0.10**	**0.10**	**0.001**
		SD	**0.14**	**0.14**	**0.001**
		RSD %	**0.14**	**31.07**	**0.145**

Method 2

JRC code	sample mass g	residue mass g	PAC %	soluble %	d
199-1	1.0473	1.0484	100.10	-0.10	0.999
199-2	1.0392	1.0402	100.10	-0.10	0.999
199-3	1.0342	1.0354	100.11	-0.11	0.999
199-4	1.0297	1.0286	99.89	0.11	1.001
199-5	1.0519	1.0535	100.15	-0.15	0.998
199-6	1.0721	1.0722	100.01	-0.01	1.000
199-7	1.06	1.0626	100.24	-0.24	0.998
199-8	1.0427	1.0426	99.99	0.01	1.000
199-9	1.0174	1.0184	100.10	-0.10	0.999
199-10	1.0227	1.0229	100.02	-0.02	1.000
		average	**100.07**	**-0.07**	**0.999**
		confidence limit	**0.07**	**0.07**	**0.001**
		SD	**0.10**	**0.10**	**0.001**
		RSD %	**0.10**	**-134.80**	**0.098**

Method 3

JRC code	sample mass g	residue mass g	insoluble %	soluble %
199-1	1.0307	0.6890	66.16	33.84
199-2	1.0524	0.7015	65.96	34.04
199-3	1.0302	0.6886	66.15	33.85
199-4	1.0196	0.6760	65.60	34.40
199-5	1.0363	0.6896	65.85	34.15
199-6	1.0457	0.7011	66.36	33.64
199-7	1.0451	0.6932	65.63	34.37
199-8	1.0245	0.6833	66.00	34.00
199-9	1.0501	0.6891	64.92	35.08
		average	**65.85**	**34.15**
		confidence limit	**0.33**	**0.33**
		SD	**0.43**	**0.43**
		RSD %	**0.65**	**1.25**

Method 4

JRC code	sample mass g	residue mass g	insoluble %	soluble %
199-1	1.079	0.7298	66.95	33.05
199-2	1.0825	0.7293	66.69	33.31
199-3	1.0691	0.7191	66.57	33.43
199-4	1.0637	0.7158	66.61	33.39
199-5	1.0511	0.7103	66.89	33.11
199-6	1.0244	0.6944	67.10	32.90
199-7	1.0361	0.7049	67.35	32.65
199-8	0.9972	0.6781	67.32	32.68
199-9	1.0566	0.7131	66.80	33.20
199-10	1.0779	0.7313	67.16	32.84
199-11	1.0283	0.6968	67.08	32.92
199-12	1.2898	0.8762	67.25	32.75
199-13	1.102	0.7438	66.81	33.19
199-14	1.1711	0.7947	67.18	32.82
		average	**66.98**	**33.02**
		confidence limit	**0.15**	**0.15**
		SD	**0.26**	**0.26**
		RSD %	**0.39**	**0.79**

Method 5

JRC code	sample mass g	residue mass g	PAC %	soluble %	d
199-1	1.0529	1.0541	100.11	-0.11	0.999
199-2	1.0129	1.0134	100.05	-0.05	1.000
199-3	1.0310	1.0317	100.07	-0.07	0.999
199-4	1.0250	1.0250	100.00	0.00	1.000
199-5	1.0409	1.0410	100.01	-0.01	1.000
199-6	1.0373	1.0377	100.04	-0.04	1.000
199-7	1.0829	1.0827	99.98	0.02	1.000
199-8	1.0499	1.0494	99.95	0.05	1.000
199-9	1.0154	1.0152	99.98	0.02	1.000
199-10	1.0571	1.0574	100.03	-0.03	1.000
		average	**100.02**	**-0.02**	**1.000**
		confidence limit	**0.03**	**0.03**	**0.0003**
		SD	**0.05**	**0.05**	**0.0005**
		RSD %	**0.05**	**-214.94**	**0.048**

Method 6

JRC code	sample mass g	residue mass g	PAC %	soluble %	d
199-1	1.0304	1.0261	99.59	0.41	1.004
199-2	1.0239	1.0202	99.64	0.36	1.004
199-3	1.0381	1.0345	99.66	0.34	1.003
199-4	1.0216	1.0178	99.63	0.37	1.004
199-5	1.0367	1.0323	99.58	0.42	1.004
199-6	1.0227	1.0198	99.72	0.28	1.003
199-7	1.0197	1.0164	99.68	0.32	1.003
199-8	1.0325	1.0283	99.60	0.40	1.004
199-9	1.0506	1.0483	99.78	0.22	1.002
199-10	1.0245	1.0202	99.58	0.42	1.004
		average	**99.65**	**0.35**	**1.004**
		confidence limit	**0.05**	**0.05**	**0.0005**
		SD	**0.07**	**0.07**	**0.001**
		RSD %	**0.07**	**18.77**	**0.067**

Method 7

JRC code	sample mass g	residue mass g	insoluble %	soluble %
199-1	1.0279	0.7145	68.85	31.15
199-2	1.037	0.7144	68.22	31.78
199-3	1.0268	0.7108	68.56	31.44
199-4	1.0722	0.7369	68.06	31.94
199-5	1.0474	0.7247	68.52	31.48
199-6	1.0465	0.7287	68.97	31.03
199-7	1.0648	0.7372	68.57	31.43
199-8	1.0529	0.7305	68.72	31.28
199-9	1.0645	0.74	68.85	31.15
199-10	1.0592	0.7311	68.36	31.64
		average	**68.57**	**31.43**
		confidence limit	**0.21**	**0.21**
		SD	**0.29**	**0.29**
		RSD %	**0.43**	**0.93**

Method 8

JRC code	sample mass g	residue mass g	PAC %	soluble %	d
199-1	1.0526	1.0456	99.34	0.66	1.007
199-2	1.0409	1.0581	101.64	-1.64	0.984
199-3	1.033	1.0447	101.12	-1.12	0.989
199-4	1.0536	1.0453	99.22	0.78	1.008
199-5	1.0417	1.0361	99.47	0.53	1.005
199-6	1.0667	1.0718	100.47	-0.47	0.995
199-7	1.0234	1.0221	99.87	0.13	1.001
199-8	1.0284	1.0528	102.35	-2.35	0.977
199-9	1.058	1.0232	96.74	3.26	1.034
199-10	1.0269	1.0093	98.30	1.70	1.017
199-11	1.1764	1.1719	99.62	0.38	1.004
199-12	1.1494	1.1439	99.53	0.47	1.005
199-13	1.0198	1.0144	99.48	0.52	1.005
199-14	1.1012	1.1047	100.31	-0.31	0.997
199-15	1.141	1.1417	100.06	-0.06	0.999
199-16	1.1264	1.125	99.88	0.12	1.001
199-17	1.1053	1.1117	100.57	-0.57	0.994
199-18	1.1576	1.1544	99.73	0.27	1.003
199-19	1.1444	1.141	99.71	0.29	1.003
		average	**99.86**	**0.14**	**1.002**
		confidence limit	**0.57**	**0.57**	**0.006**
		SD	**1.19**	**1.19**	**0.012**
		RSD %	**1.19**	**870.98**	**1.208**

Method 9

JRC code	sample mass g	residue mass g	PAC %	soluble %	d
199-1	1.0679	1.0625	99.50	0.50	1.005
199-2	1.0375	1.0345	99.71	0.29	1.003
199-3	1.013	1.0057	99.29	0.71	1.007
199-4	0.9963	0.9909	99.46	0.54	1.005
199-5	1.0477	1.0418	99.44	0.56	1.006
199-6	1.0329	1.0278	99.51	0.49	1.005
199-7	1.0429	1.0408	99.80	0.20	1.002
199-8	1.0706	1.0658	99.56	0.44	1.005
199-9	1.0447	1.0426	99.80	0.20	1.002
		average	**99.56**	**0.44**	**1.004**
		confidence limit	**0.13**	**0.13**	**0.001**
		SD	**0.17**	**0.17**	**0.002**
		RSD %	**0.18**	**40.00**	**0.177**

Method 10

JRC code	sample mass g	residue mass g	PAC %	soluble %	d
199-1	1.0133	1.0133	100.00	0.00	1.000
199-2	1.0062	1.0057	99.95	0.05	1.000
199-3	1.0256	1.0248	99.92	0.08	1.001
199-4	1.0121	1.0101	99.80	0.20	1.002
199-5	1.0208	1.0194	99.86	0.14	1.001
199-6	1.0301	1.0294	99.93	0.07	1.001
199-7	0.9998	0.9988	99.90	0.10	1.001
199-8	1.011	1.0099	99.89	0.11	1.001
199-9	1.004	1.0024	99.84	0.16	1.002
199-10	1.0062	1.0057	99.95	0.05	1.000
		average	**99.91**	**0.09**	**1.001**
		confidence limit	**0.04**	**0.04**	**0.0004**
		SD	**0.06**	**0.06**	**0.001**
		RSD %	**0.06**	**61.70**	**0.059**

Method 11

JRC code	sample mass g	residue mass g	PAC %	soluble %	d
199-1	1.0624	1.0387	97.79	2.21	1.023
199-2	1.1102	1.0863	97.87	2.13	1.022
199-3	1.0455	1.0228	97.85	2.15	1.022
199-4	1.1353	1.1099	97.78	2.22	1.023
199-5	1.0223	0.9992	97.76	2.24	1.023
199-6	0.9119	0.8917	97.81	2.19	1.023
199-7	0.8517	0.8325	97.77	2.23	1.023
199-8	0.9301	0.9096	97.82	2.18	1.023
199-9	1.0053	0.984	97.90	2.10	1.022
		average	**97.82**	**2.18**	**1.023**
		confidence limit	**0.04**	**0.04**	**0.0004**
		SD	**0.05**	**0.05**	**0.001**
		RSD %	**0.05**	**2.18**	**0.049**

Method 13

JRC code	sample mass g	residue mass g	insoluble %	soluble %
199-1	1.053	0.4145	40.11	59.89
199-2	0.9973	0.3968	40.53	59.47
199-3	1.0389	0.41034	40.24	59.76
199-4	1.2188	0.4783	39.99	60.01
199-5	1.0133	0.4006	40.28	59.72
199-6	1.0329	0.4065	40.10	59.90
199-7	1.0126	0.4042	40.66	59.34
199-8	1.0413	0.4071	39.84	60.16
		average	**40.22**	**59.78**
		confidence limit	**0.23**	**0.23**
		SD	**0.27**	**0.27**
		RSD %	**0.68**	**0.46**

Method 14

JRC code	sample mass g	residue mass g	insoluble %	soluble %
199-1	1.0359	0.7	66.89	33.11
199-2	1.1229	0.7551	66.56	33.44
199-3	1.0899	0.7341	66.67	33.33
199-4	1.0249	0.6901	66.65	33.35
199-5	1.1063	0.7454	66.69	33.31
199-6	1.0965	0.7376	66.58	33.42
199-7	1.0297	0.6934	66.65	33.35
199-8	1.0207	0.6819	66.11	33.89
		average	**66.60**	**33.40**
		confidence limit	**0.18**	**0.18**
		SD	**0.22**	**0.22**
		RSD %	**0.33**	**0.66**

Method 15

JRC code	sample mass g	residue mass g	insoluble %	soluble %
199-1	1.0484	0.4082	39.68	60.32
199-2	0.9972	0.3913	39.98	60.02
199-3	1.1604	0.4336	38.10	61.90
199-4	1.1474	0.4525	40.18	59.82
199-5	1.0651	0.4144	39.65	60.35
199-6	1.1387	0.4787	42.80	57.20
199-7	1.1689	0.5033	43.82	56.18
199-8	1.2007	0.4619	39.21	60.79
199-9	1.2254	0.4778	39.73	60.27
		average	**40.35**	**59.65**
		confidence limit	**1.38**	**1.38**
		SD	**1.80**	**1.80**
		RSD %	**4.46**	**3.02**

Method 16

JRC code	sample mass g	residue mass g	insoluble %	soluble %
199-1	1.1414	0.7490	64.92	35.08
199-2	1.1199	0.7375	65.15	34.85
199-3	1.1946	0.7832	64.86	35.14
199-4	1.2122	0.7867	64.19	35.81
199-5	1.1229	0.7319	64.47	35.53
199-6	1.1241	0.7385	64.99	35.01
199-7	1.1334	0.7461	65.13	34.87
199-8	1.2088	0.7974	65.27	34.73
199-9	1.0901	0.7154	64.92	35.08
199-10	1.1170	0.7346	65.06	34.94
199-11	1.1259	0.7386	64.90	35.10
199-12	1.1094	0.7278	64.90	35.10
199-13	1.1338	0.7420	64.74	35.26
199-14	1.0351	0.6782	64.82	35.18
199-15	1.1628	0.7624	64.86	35.14
199-16	1.0895	0.7128	64.72	35.28
199-17	1.1087	0.7264	64.81	35.19
199-18	1.0774	0.7063	64.85	35.15
199-19	1.1229	0.7349	64.74	35.26
199-20	1.1552	0.7505	64.26	35.74
199-21	1.0829	0.7098	64.84	35.16
199-22	1.0483	0.6867	64.80	35.20
199-23	1.0191	0.6674	64.78	35.22
199-24	1.0405	0.6815	64.79	35.21
199-25	1.0162	0.6659	64.82	35.18
		average	**64.82**	**35.18**
		confidence limit	**0.10**	**0.10**
		SD	**0.24**	**0.24**
		RSD %	**0.37**	**0.68**

- ***Ventilated oven***

Method 11

JRC code	sample mass g	residue mass g	PAC %	soluble %	d
199-1	1.0049	0.9744	96.99	3.01	1.031
199-2	1.0328	1.0013	96.98	3.02	1.031
199-3	1.0367	1.0054	97.01	2.99	1.031
199-4	1.0196	0.9883	96.96	3.04	1.032
199-5	1.0117	0.9815	97.04	2.96	1.031
199-6	0.9934	0.9632	96.99	3.01	1.031
199-7	0.9973	0.9675	97.04	2.96	1.031
199-8	1.0178	0.9834	96.65	3.35	1.035
199-9	1.0084	0.9775	96.97	3.03	1.032
199-10	1.0106	0.9764	96.65	3.35	1.035
		average	**96.93**	**3.07**	**1.032**
		confidence limit	**0.11**	**0.11**	**0.001**
		SD	**0.15**	**0.15**	**0.002**
		RSD %	**0.15**	**4.85**	**0.156**

PAC 20 % (sample 233)

Method 1

JRC code	sample mass g	residue mass g	PAC %	soluble %	d
233-1	1.1205	1.1179	99.77	0.23	1.002
233-2	1.0342	1.0320	99.79	0.21	1.002
233-3	1.0476	1.0460	99.85	0.15	1.002
233-4	1.0438	1.0430	99.92	0.08	1.001
233-5	1.0827	1.0796	99.72	0.28	1.003
233-6	1.0382	1.0401	100.18	-0.18	0.998
233-7	1.1399	1.1411	100.10	-0.10	0.999
233-8	1.0615	1.0567	99.55	0.45	1.005
233-9	1.0750	1.0723	99.75	0.25	1.003
233-10	1.1427	1.1408	99.84	0.16	1.002
233-11	1.0696	1.0671	99.77	0.23	1.002
233-12	1.0732	1.0708	99.78	0.22	1.002
233-13	1.0731	1.0727	99.96	0.04	1.000
233-14	1.1219	1.1250	100.27	-0.27	0.997
233-15	0.9855	0.9814	99.59	0.41	1.004
233-16	1.0412	1.0402	99.90	0.10	1.001
233-17	1.1177	1.1136	99.64	0.36	1.004
233-18	0.9850	0.9820	99.70	0.30	1.003
233-19	1.1537	1.1494	99.63	0.37	1.004
		average	**99.83**	**0.17**	**1.002**
		confidence limit	**0.09**	**0.09**	**0.001**
		SD	**0.20**	**0.20**	**0.002**
		RSD %	**0.20**	**113.15**	**0.198**

Method 2

JRC code	sample mass g	residue mass g	PAC %	soluble %	d
280-1	1.3362	1.3340	99.84	0.16	1.002
280-2	1.2788	1.2770	99.86	0.14	1.001
280-3	1.3206	1.3188	99.87	0.13	1.001
280-4	1.2948	1.2931	99.87	0.13	1.001
280-5	1.3070	1.3056	99.89	0.11	1.001
280-6	1.2574	1.2558	99.87	0.13	1.001
280-7	1.3057	1.3037	99.85	0.15	1.002
280-8	1.2885	1.2867	99.86	0.14	1.001
280-9	1.3203	1.3185	99.87	0.13	1.001
280-10	1.2802	1.2778	99.81	0.19	1.002
280-11	1.3161	1.3144	99.87	0.13	1.001
280-12	1.2568	1.2555	99.90	0.10	1.001
280-13	1.2681	1.2662	99.85	0.15	1.002
280-14	1.3302	1.3279	99.83	0.17	1.002
280-15	1.3001	1.2980	99.84	0.16	1.002
280-16	1.3002	1.2982	99.85	0.15	1.002
280-17	1.3140	1.3123	99.87	0.13	1.001
280-18	1.2716	1.2702	99.89	0.11	1.001
280-19	1.3370	1.3350	99.85	0.15	1.001
280-20	1.3273	1.3249	99.82	0.18	1.002
		average	**99.86**	**0.14**	**1.001**
		confidence limit	**0.01**	**0.01**	**0.0001**
		SD	**0.02**	**0.02**	**0.0002**
		RSD %	**0.02**	**16.20**	**0.023**

Method 3

JRC code	sample mass g	residue mass g	insoluble %	soluble %
233-1	1.0853	0.8977	82.27	17.73
233-2	1.1022	0.9105	82.16	17.84
233-3	1.1819	0.9767	82.19	17.81
233-4	1.1553	0.9535	82.08	17.92
233-5	1.1751	0.9704	82.13	17.87
233-6	1.1828	0.9754	82.01	17.99
233-7	1.1723	0.9679	82.11	17.89
233-8	1.1032	0.9116	82.18	17.82
233-9	1.2365	1.0269	82.61	17.39
233-10	1.1623	0.9652	82.60	17.40
		average	**82.23**	**17.77**
		confidence limit	**0.15**	**0.10**
		SD	**0.21**	**0.21**
		RSD %	**0.25**	**1.16**

Method 4

JRC code	sample mass g	residue mass g	insoluble %	soluble %
233-1	0.8765	0.8331	94.90	5.10
233-2	0.9991	0.9416	94.07	5.93
233-3	1.0588	1.0040	94.67	5.33
233-4	1.0185	0.9641	94.50	5.50
233-5	1.0712	1.0138	94.48	5.52
233-6	0.9277	0.8735	93.98	6.02
233-7	0.9117	0.8703	95.32	4.68
233-8	0.6375	0.6037	94.54	5.46
233-9	1.1050	1.0526	95.12	4.88
233-10	1.0238	0.9685	94.44	5.56
		average	**94.60**	**5.40**
		confidence limit	**0.30**	**0.30**
		SD	**0.42**	**0.42**
		RSD %	**0.44**	**7.79**

Method 5

JRC code	sample mass g	residue mass g	PAC %	soluble %	d
233-1	1.1266	1.1246	99.82	0.18	1.002
233-2	1.0043	1.0037	99.94	0.06	1.001
233-3	1.1639	1.162	99.84	0.16	1.002
233-4	1.1527	1.1518	99.92	0.08	1.001
233-5	0.9977	1.0021	100.44	-0.44	0.996
233-6	1.1102	1.1089	99.88	0.12	1.001
233-7	1.1402	1.1387	99.87	0.13	1.001
233-8	1.0718	1.0790	100.67	-0.67	0.993
233-9	1.3688	1.3668	99.86	0.14	1.001
233-10	1.0482	1.0578	100.91	-0.91	0.991
233-11	1.0051	1.0166	101.13	-1.13	0.989
233-12	1.0977	1.0982	100.05	-0.05	1.000
233-13	1.1259	1.1250	99.92	0.08	1.001
233-14	0.9967	1.0065	100.97	-0.97	0.990
233-15	1.0622	1.0600	99.79	0.21	1.002
233-16	1.2002	1.1988	99.88	0.12	1.001
233-17	1.1545	1.1603	100.50	-0.50	0.995
233-18	1.0908	1.1096	101.71	-1.71	0.983
233-19	1.0735	1.0721	99.87	0.13	1.001
233-20	0.9736	0.9746	100.10	-0.10	0.999
		average	**100.25**	**-0.25**	**1.00**
		confidence limit	**0.26**	**0.26**	**0.003**
		SD	**0.55**	**0.55**	**0.005**
		RSD %	**0.55**	**-217.27**	**0.551**

Method 6

JRC code	sample mass g	residue mass g	PAC %	soluble %	d
233-1	1.0750	1.0722	99.74	0.26	1.003
233-2	1.0196	1.0177	99.82	0.18	1.002
233-3	1.0369	1.0373	100.04	-0.04	1.000
233-4	1.0235	1.0195	99.61	0.39	1.004
233-5	1.0106	1.0126	100.20	-0.20	0.998
233-6	1.0555	1.0552	99.97	0.03	1.000
233-7	1.0235	1.0211	99.77	0.23	1.002
233-8	1.0675	1.0670	99.95	0.05	1.000
233-9	1.0372	1.0347	99.76	0.24	1.002
233-10	1.0507	1.0487	99.81	0.19	1.002
233-11	1.0301	1.0273	99.73	0.27	1.003
233-12	1.0218	1.0200	99.83	0.17	1.002
233-13	1.0400	1.0369	99.70	0.30	1.003
233-14	1.0284	1.0298	100.13	-0.13	0.999
233-15	1.0332	1.0282	99.52	0.48	1.005
233-16	1.0407	1.0380	99.74	0.26	1.003
233-17	1.0684	1.0653	99.71	0.29	1.003
233-18	1.0220	1.0220	100.00	0.00	1.000
233-19	1.0732	1.0731	99.99	0.01	1.000
233-20	1.0329	1.0299	99.71	0.29	1.003
		average	**99.84**	**0.16**	**1.002**
		confidence limit	**0.08**	**0.08**	**0.001**
		SD	**0.17**	**0.17**	**0.002**
		RSD %	**0.17**	**107.36**	**0.177**

Method 7

JRC code	sample mass g	residue mass g	PAC %	soluble %	d
233-1	1.0542	1.0476	99.38	0.62	1.006
233-2	0.9976	0.9907	99.32	0.68	1.007
233-3	1.176	1.1696	99.46	0.54	1.005
233-4	1.1490	1.1414	99.35	0.65	1.007
233-5	1.0722	1.067	99.52	0.48	1.005
233-6	0.9402	0.9326	99.20	0.80	1.008
233-7	1.0286	1.0202	99.19	0.81	1.008
233-8	0.9250	0.9186	99.31	0.69	1.007
233-9	1.0294	1.0236	99.44	0.56	1.006
233-10	1.2063	1.1983	99.34	0.66	1.007
233-11	1.1271	1.1219	99.54	0.46	1.005
233-12	0.9628	0.9551	99.21	0.79	1.008
233-13	1.1155	1.1102	99.53	0.47	1.005
233-14	1.2035	1.1968	99.45	0.55	1.006
233-15	1.0572	1.0498	99.31	0.69	1.007
233-16	1.1463	1.1402	99.47	0.53	1.005
233-17	1.0396	1.0336	99.43	0.57	1.006
233-18	1.002	0.9963	99.44	0.56	1.006
233-19	0.9210	0.9144	99.29	0.71	1.007
233-20	1.1212	1.1156	99.51	0.49	1.005
		average	**99.38**	**0.62**	**1.006**
		confidence limit	**0.05**	**0.05**	**0.001**
		SD	**0.11**	**0.11**	**0.001**
		RSD %	**0.11**	**18.07**	**0.113**

Method 8

JRC code	sample mass g	residue mass g	PAC %	soluble %	d
280-1	1.2915	1.2879	99.72	0.28	1.003
280-2	1.2577	1.2539	99.70	0.30	1.003
280-3	1.3515	1.3467	99.65	0.35	1.004
280-4	1.2673	1.2636	99.71	0.29	1.003
280-5	1.3120	1.3086	99.74	0.26	1.003
280-6	1.2487	1.2453	99.73	0.27	1.003
280-7	1.2528	1.2498	99.76	0.24	1.002
280-8	1.2936	1.2900	99.72	0.28	1.003
280-9	1.2892	1.2854	99.71	0.29	1.003
280-10	1.3414	1.3375	99.71	0.29	1.003
280-11	1.2416	1.2390	99.79	0.21	1.002
280-12	1.3607	1.3574	99.76	0.24	1.002
280-13	1.3107	1.3079	99.79	0.21	1.002
280-14	1.3062	1.3032	99.77	0.23	1.002
280-15	1.3278	1.3242	99.73	0.27	1.003
280-16	1.2769	1.2731	99.71	0.29	1.003
280-17	1.2978	1.2935	99.67	0.33	1.003
280-18	1.2831	1.2793	99.71	0.29	1.003
280-19	1.3582	1.3550	99.77	0.23	1.002
280-20	1.2959	1.2924	99.73	0.27	1.003
		average	**99.73**	**0.27**	**1.003**
		confidence limit	**0.02**	**0.02**	**0.0002**
		SD	**0.04**	**0.04**	**0.0004**
		RSD %	**0.04**	**13.67**	**0.037**

Method 9

JRC code	sample mass g	residue mass g	PAC %	soluble %	d
233-1	1.0602	1.0574	99.74	0.26	1.003
233-2	1.0461	1.0433	99.73	0.27	1.003
233-3	1.0726	1.0675	99.53	0.47	1.005
233-4	1.2540	1.2520	99.84	0.16	1.002
233-5	1.0442	1.0432	99.91	0.09	1.001
233-6	1.0376	1.0363	99.88	0.12	1.001
233-7	1.0448	1.0441	99.93	0.07	1.001
233-8	1.0489	1.0459	99.72	0.28	1.003
233-9	1.0331	1.0302	99.72	0.28	1.003
233-10	1.0260	1.0230	99.71	0.29	1.003
233-11	1.0476	1.0525	100.46	-0.46	0.995
233-12	1.0554	1.0572	100.17	-0.17	0.998
233-13	1.0538	1.0544	100.06	-0.06	0.999
233-14	1.0664	1.0641	99.79	0.21	1.002
233-15	1.0342	1.0339	99.97	0.03	1.000
233-16	1.0666	1.0672	100.06	-0.06	0.999
233-17	1.0398	1.0418	100.19	-0.19	0.998
233-18	1.0540	1.0538	99.98	0.02	1.000
233-19	1.0460	1.0432	99.73	0.27	1.003
		average	**99.90**	**0.10**	**1.001**
		confidence limit	**0.11**	**0.11**	**0.001**
		SD	**0.22**	**0.22**	**0.002**
		RSD %	**0.22**	**222.02**	**0.222**

Method 10

JRC code	sample mass g	residue mass g	PAC %	soluble %	d
233-1	1.0170	1.0076	99.08	0.92	1.009
233-2	1.0329	1.0449	101.15	-1.15	0.989
233-3	1.0067	1.0118	100.50	-0.50	0.995
233-4	1.0362	1.0334	99.73	0.27	1.003
233-5	1.0034	1.0230	101.93	-1.93	0.981
233-6	1.0136	1.0126	99.90	0.10	1.001
233-7	1.0082	1.0066	99.84	0.16	1.002
233-8	1.0588	1.0716	101.20	-1.20	0.988
233-9	1.0538	1.0710	101.62	-1.62	0.984
233-10	1.0429	1.0521	100.87	-0.87	0.991
233-11	1.0526	1.0548	100.21	-0.21	0.998
233-12	1.0456	1.0534	100.74	-0.74	0.993
233-13	1.0246	1.0262	100.15	-0.15	0.998
233-14	1.0005	1.0040	100.35	-0.35	0.997
233-15	1.0095	1.0076	99.81	0.19	1.002
233-16	1.0055	1.0087	100.32	-0.32	0.997
233-17	0.9974	0.9998	100.24	-0.24	0.998
233-18	1.0139	1.0117	99.79	0.21	1.002
233-19	0.9950	0.9925	99.75	0.25	1.003
233-20	0.9436	0.9455	100.20	-0.20	0.998
		average	**100.37**	**-0.37**	**0.996**
		confidence limit	**0.33**	**0.33**	**0.003**
		SD	**0.70**	**0.70**	**0.007**
		RSD %	**0.70**	**-190.62**	**0.705**

Method 11

JRC code	sample mass g	residue mass g	PAC %	soluble %	d
280-1	1.2600	1.2526	99.42	0.58	1.006
280-2	1.2436	1.2365	99.43	0.57	1.006
280-3	1.4551	1.4453	99.33	0.67	1.007
280-4	1.3490	1.3403	99.36	0.64	1.006
280-5	1.3001	1.2918	99.37	0.63	1.006
280-6	1.3167	1.3089	99.41	0.59	1.006
280-7	1.2560	1.2480	99.37	0.63	1.006
280-8	1.3444	1.3368	99.44	0.56	1.006
280-9	1.1550	1.1474	99.35	0.65	1.007
280-10	1.2414	1.2343	99.43	0.57	1.006
280-11	1.3404	1.3317	99.36	0.64	1.007
280-12	1.2655	1.2592	99.51	0.49	1.005
280-13	1.2478	1.2408	99.44	0.56	1.006
280-14	1.3654	1.3571	99.40	0.60	1.006
280-15	1.4032	1.3946	99.39	0.61	1.006
280-16	1.2686	1.2614	99.44	0.56	1.006
280-17	1.3098	1.3015	99.37	0.63	1.006
280-18	1.1754	1.1680	99.38	0.62	1.006
280-19	1.2743	1.2665	99.39	0.61	1.006
280-20	1.3619	1.3531	99.36	0.64	1.007
		average	**99.40**	**0.60**	**1.006**
		confidence limit	**0.02**	**0.02**	**0.0002**
		SD	**0.04**	**0.04**	**0.0004**
		RSD %	**0.04**	**7.10**	**0.043**

Method 14

JRC code	sample mass	residue mass	PAC	soluble	d
	g	g	%	%	
233-1	1.0502	1.0450	99.51	0.49	1.005
233-2	1.0181	1.0118	99.39	0.61	1.006
233-3	1.0542	1.0431	98.96	1.04	1.011
233-4	1.1314	1.1220	99.18	0.82	1.008
233-5	0.9022	0.8954	99.25	0.75	1.008
233-6	0.9869	0.9801	99.32	0.68	1.007
233-7	1.0571	1.0505	99.38	0.62	1.006
233-8	1.0225	1.0214	99.89	0.11	1.001
233-9	1.0267	1.0204	99.39	0.61	1.006
233-10	1.0281	1.0227	99.48	0.52	1.005
233-11	1.0449	1.0387	99.41	0.59	1.006
233-12	1.0124	1.0056	99.33	0.67	1.007
233-13	1.0421	1.0357	99.39	0.61	1.006
233-14	1.0645	1.0543	99.05	0.95	1.010
233-15	1.1128	1.1041	99.23	0.77	1.008
233-16	0.9866	0.9783	99.17	0.83	1.008
233-17	1.0626	1.0536	99.16	0.84	1.009
233-18	1.0038	0.9960	99.23	0.77	1.008
233-19	0.8853	0.8768	99.05	0.95	1.010
233-20	1.1553	1.1464	99.24	0.76	1.008
		average	**99.30**	**0.70**	**1.01**
		confidence limit	**0.10**	**0.10**	**0.001**
		SD	**0.20**	**0.20**	**0.002**
		RSD %	**0.20**	**29.06**	**0.206**

Method 16

JRC code	sample mass	residue mass	insoluble	soluble
	g	g	%	%
233-1	1.0752	0.8779	81.18	18.82
233-2	1.0141	0.8303	81.41	18.59
233-3	1.0056	0.8201	81.08	18.92
233-4	1.0411	0.8494	81.12	18.88
233-5	0.9986	0.8143	81.07	18.93
233-6	0.9822	0.8014	81.12	18.88
233-7	1.0237	0.8352	81.12	18.88
233-8	1.0526	0.8590	81.14	18.86
233-9	1.0445	0.8522	81.12	18.88
233-10	1.0273	0.8382	81.12	18.88
		average	**81.15**	**18.85**
		confidence limit	**0.07**	**0.05**
		SD	**0.10**	**0.10**
		RSD %	**0.12**	**0.51**

PAC 40 % (sample 266)

method 11

JRC code	sample mass	residue mass	insoluble	soluble
	g	g	%	%
266-1	0.9931	0.6597	66.07	33.93
266-2	1.0022	0.6674	66.24	33.76
266-3	1.0371	0.6810	65.29	34.71
266-4	0.9873	0.6394	64.36	35.64
266-5	0.9892	0.6525	65.59	34.41
		average	**65.51**	**34.49**
		confidence limit	**0.92**	**0.92**
		SD	**0.74**	**0.74**
		RSD %	**1.14**	**2.16**

PAC 40 % (sample 281)

method 11

JRC code	sample mass g	residue mass g	insoluble %	soluble %
281-1	1.0585	0.9252	88.38	11.62
281-2	1.1600	0.9424	82.20	17.80
281-3	1.2256	0.9320	76.98	23.02
		average	**82.52**	**17.48**
		confidence limit	**14.18**	**14.18**
		SD	**5.71**	**5.71**
		RSD %	**6.92**	**32.66**

Quantification of PA6 in PAC

Elemental analysis

PAC 5 %– 40 % (samples 195 – 199, 233)

JRC code	nitrogen %	carbon %	hydrogen %
195-1	0.608	84.100	14.701
195-2	1.091	83.902	14.728
average	**0.850**	**84.001**	**14.715**
confidence limit	**3.069**	**1.258**	**0.172**
SD	**0.342**	**0.140**	**0.019**
RSD %	**40.204**	**0.167**	**0.130**

JRC code	nitrogen %	carbon %	hydrogen %
196-1	1.288	83.095	14.250
196-2	1.272	83.013	14.325
average	**1.280**	**83.054**	**14.288**
confidence limit	**0.102**	**0.521**	**0.476**
SD	**0.011**	**0.058**	**0.053**
RSD %	**0.884**	**0.070**	**0.371**

JRC code	nitrogen %	carbon %	hydrogen %
197-1	2.371	81.020	13.939
197-2	2.364	80.801	13.880
average	**2.368**	**80.911**	**13.910**
confidence limit	**0.044**	**1.391**	**0.375**
SD	**0.005**	**0.155**	**0.042**
RSD %	**0.209**	**0.191**	**0.300**

JRC code	nitrogen %	carbon %	hydrogen %
198-1	3.402	78.746	13.426
198-2	3.393	78.697	13.431
average	**3.398**	**78.722**	**13.429**
confidence limit	**0.057**	**0.311**	**0.032**
SD	**0.006**	**0.035**	**0.004**
RSD %	**0.187**	**0.044**	**0.026**

JRC code	nitrogen %	carbon %	hydrogen %
199-1	4.367	77.103	13.197
199-2	4.369	77.115	13.182
average	**4.368**	**77.109**	**13.190**
confidence limit	**0.013**	**0.076**	**0.095**
SD	**0.001**	**0.008**	**0.011**
RSD %	**0.032**	**0.011**	**0.080**

JRC code	nitrogen %	carbon %	hydrogen %
233-1	2.368	80.624	13.872
233-2	2.373	80.593	13.819
average	**2.371**	**80.609**	**13.846**
confidence limit	**0.032**	**0.197**	**0.337**
SD	**0.004**	**0.022**	**0.037**
RSD %	**0.149**	**0.027**	**0.271**

polyamide (sample 193)

JRC code	nitrogen %	carbon %	hydrogen %
193-1	11.943	62.265	9.970
193-2	11.945	62.292	9.984
average	**11.944**	**62.279**	**9.977**
confidence limit	**0.013**	**0.172**	**0.089**
SD	**0.001**	**0.019**	**0.010**
RSD %	**0.012**	**0.031**	**0.099**

Hydrolysis method

PAC 5 %– 40 % (samples 195 - 199, 233)

JRC code	sample mass g	residue mass g	insoluble %	soluble %
195-1	1.0140	0.9858	97.13	2.87
195-2	1.0324	1.0036	97.12	2.88
195-3	1.0129	0.9731	95.95	4.05
195-4	1.0135	0.9840	97.00	3.00
195-5	1.0103	0.9769	96.59	3.41
		average	**96.76**	**3.24**
		confidence limit	**0.62**	**0.62**
		SD	**0.50**	**0.50**
		RSD %	**0.52**	**15.52**

JRC code	sample mass g	residue mass g	insoluble %	soluble %
196-1	1.1893	1.0971	92.02	7.98
196-2	1.0504	0.9710	92.22	7.78
196-3	1.1120	1.0269	92.12	7.88
196-4	1.0871	1.0046	92.19	7.81
196-5	1.1479	1.0539	91.57	8.43
		average	**92.03**	**7.97**
		confidence limit	**0.33**	**0.33**
		SD	**0.26**	**0.26**
		RSD %	**0.29**	**3.31**

JRC code	sample mass g	residue mass g	insoluble %	soluble %
197-1	1.1014	0.9073	81.92	18.08
197-2	1.0614	0.8761	82.09	17.91
197-3	1.0829	0.8890	81.63	18.37
197-4	1.0962	0.8970	81.36	18.64
		average	**81.75**	**18.25**
		confidence limit	**0.51**	**0.51**
		SD	**0.32**	**0.32**
		RSD %	**0.39**	**1.76**

JRC code	sample mass g	residue mass g	insoluble %	soluble %
198-1	1.0907	0.8093	73.60	26.40
198-2	1.0007	0.7515	74.51	25.49
198-3	1.0738	0.8030	74.19	25.81
198-4	0.9630	0.7269	74.90	25.10
198-5	0.9836	0.7392	74.57	25.43
		average	**74.35**	**25.65**
		confidence limit	**0.61**	**0.61**
		SD	**0.49**	**0.49**
		RSD %	**0.66**	**1.92**

JRC code	sample mass g	residue mass g	insoluble %	soluble %
199-1	1.0138	0.6590	64.29	35.71
199-2	1.0158	0.6577	64.03	35.97
199-3	0.9983	0.6414	63.53	36.47
199-4	1.0383	0.6701	63.82	36.18
199-5	1.0203	0.6608	64.05	35.95
		average	**63.95**	**36.05**
		confidence limit	**0.35**	**0.35**
		SD	**0.29**	**0.29**
		RSD %	**0.45**	**0.79**

JRC code	sample mass g	residue mass g	insoluble %	soluble %
233-1	1.0300	0.8406	81.14	18.86
233-2	1.0307	0.8455	81.57	18.43
233-3	1.0335	0.8444	81.23	18.77
233-4	1.0601	0.8657	81.19	18.81
		average	**81.28**	**18.72**
		confidence limit	**0.31**	**0.31**
		SD	**0.19**	**0.19**
		RSD %	**0.24**	**1.04**

Method 16 of Directive 96/73/EC

PAC 5 %– 40 % (samples 195 – 199, 233)

JRC code	sample mass g	residue mass g	insoluble %	soluble %
195-1	1.0997	1.0550	95.81	4.19
195-2	1.1465	1.1000	95.82	4.18
195-3	1.0507	1.0081	95.82	4.18
195-4	1.0191	0.9766	95.70	4.30
195-5	1.1037	1.0582	95.75	4.25
195-6	1.0529	1.0098	95.78	4.22
195-7	1.0367	0.9942	95.78	4.22
195-8	1.0145	0.9736	95.85	4.15
195-9	1.0177	0.9769	95.87	4.13
195-10	1.0034	0.9630	95.85	4.15
195-11	1.2244	1.1746	95.81	4.19
195-12	1.1043	1.0594	95.81	4.19
195-13	1.0329	0.9908	95.80	4.20
195-14	1.0355	0.9929	95.76	4.24
195-15	1.3166	1.2629	95.80	4.20
195-16	1.2527	1.2016	95.80	4.20
195-17	1.2959	1.2432	95.81	4.19
195-18	1.2123	1.1626	95.78	4.22
195-19	1.0118	0.9702	95.76	4.24
195-20	1.1973	1.1485	95.80	4.20
		average	**95.80**	**4.20**
		confidence limit	**0.02**	**0.02**
		SD	**0.04**	**0.04**
		RSD %	**0.04**	**0.89**

JRC code	sample mass g	residue mass g	insoluble %	soluble %
196-1	1.1896	1.0863	91.07	8.93
196-2	1.1124	1.0154	91.03	8.97
196-3	1.0414	0.9505	91.02	8.98
196-4	1.1320	1.0331	91.01	8.99
196-5	1.0997	1.0042	91.07	8.93
196-6	1.0291	0.9391	91.00	9.00
196-7	1.0413	0.9502	91.00	9.00
196-8	1.1628	1.0613	91.02	8.98
196-9	0.9849	0.8991	91.04	8.96
196-10	1.0764	0.9830	91.07	8.93
196-11	1.1791	1.0772	91.11	8.89
196-12	1.0434	0.9523	91.02	8.98
196-13	1.0871	0.9937	91.16	8.84
196-14	1.0579	0.9666	91.12	8.88
196-15	1.0772	0.9840	91.10	8.90
196-16	1.0764	0.9829	91.06	8.94
196-17	1.1220	1.0242	91.03	8.97
196-18	1.0661	0.9740	91.11	8.89
196-19	1.1686	1.0672	91.07	8.93
		average	**91.06**	**8.94**
		confidence limit	**0.02**	**0.02**
		SD	**0.05**	**0.05**
		RSD %	**0.05**	**0.51**

JRC code	sample mass g	residue mass g	insoluble %	soluble %
197-1	1.13	0.93	81.51	18.49
197-2	1.11	0.90	80.70	19.30
197-3	1.13	0.93	81.44	18.56
197-4	1.22	1.00	81.31	18.69
197-5	1.11	0.90	80.77	19.23
197-6	1.12	0.92	81.48	18.52
197-7	1.22	1.00	81.31	18.69
197-8	1.15	0.93	80.77	19.23
197-9	1.18	0.96	81.33	18.67
197-10	1.16	0.94	81.14	18.86
197-11	1.06	0.86	81.34	18.66
197-12	1.00	0.82	81.27	18.73
197-13	1.05	0.86	81.36	18.64
197-14	1.02	0.83	81.29	18.71
197-15	1.03	0.84	81.29	18.71
197-16	1.00	0.81	81.14	18.86
197-17	1.02	0.83	81.20	18.80
197-18	1.03	0.84	81.25	18.75
197-19	1.00	0.82	81.21	18.79
197-20	1.02	0.83	81.23	18.77
		average	**81.22**	**18.78**
		confidence limit	**0.11**	**0.11**
		SD	**0.22**	**0.22**
		RSD %	**0.28**	**1.20**

JRC code	sample mass g	residue mass g	insoluble %	soluble %
198-1	1.1734	0.8581	72.51	27.49
198-2	1.1752	0.8596	72.53	27.47
198-3	1.2382	0.9057	72.53	27.47
198-4	1.1973	0.8744	72.41	27.59
198-5	1.1727	0.8578	72.53	27.47
198-6	1.2141	0.8875	72.48	27.52
198-7	1.1911	0.8692	72.36	27.64
198-8	1.2349	0.9017	72.40	27.60
198-9	1.1756	0.8582	72.38	27.62
198-10	1.2645	0.9226	72.34	27.66
198-11	1.0265	0.7504	72.49	27.51
198-12	1.0410	0.7600	72.39	27.61
198-13	1.0300	0.7509	72.28	27.72
198-14	1.0264	0.7493	72.39	27.61
198-15	1.0322	0.7534	72.37	27.63
198-16	1.0398	0.7582	72.30	27.70
198-17	1.0380	0.7574	72.35	27.65
198-18	1.0381	0.7569	72.29	27.71
198-19	1.0365	0.7545	72.17	27.83
198-20	1.0328	0.7537	72.36	27.64
		average	**72.39**	**27.61**
		confidence limit	**0.05**	**0.05**
		SD	**0.10**	**0.10**
		RSD %	**0.13**	**0.35**

JRC code	sample mass g	residue mass g	insoluble %	soluble %
199-1	1.1414	0.7490	64.92	35.08
199-2	1.1199	0.7375	65.15	34.85
199-3	1.1946	0.7832	64.86	35.14
199-4	1.2122	0.7867	64.19	35.81
199-5	1.1229	0.7319	64.47	35.53
199-6	1.1241	0.7385	64.99	35.01
199-7	1.1334	0.7461	65.13	34.87
199-8	1.2088	0.7974	65.27	34.73
199-9	1.0901	0.7154	64.92	35.08
199-10	1.1170	0.7346	65.06	34.94
199-11	1.1259	0.7386	64.90	35.10
199-12	1.1094	0.7278	64.90	35.10
199-13	1.1338	0.7420	64.74	35.26
199-14	1.0351	0.6782	64.82	35.18
199-15	1.1628	0.7624	64.86	35.14
199-16	1.0895	0.7128	64.72	35.28
199-17	1.1087	0.7264	64.81	35.19
199-18	1.0774	0.7063	64.85	35.15
199-19	1.1229	0.7349	64.74	35.26
199-20	1.1552	0.7505	64.26	35.74
199-21	1.0829	0.7098	64.84	35.16
199-22	1.0483	0.6867	64.80	35.20
199-23	1.0191	0.6674	64.78	35.22
199-24	1.0405	0.6815	64.79	35.21
199-25	1.0162	0.6659	64.82	35.18
		average	**64.82**	**35.18**
		confidence limit	**0.10**	**0.10**
		SD	**0.24**	**0.24**
		RSD %	**0.37**	**0.68**

JRC code	sample mass g	residue mass g	insoluble %	soluble %
233-1	1.0752	0.8779	81.18	18.82
233-2	1.0141	0.8303	81.41	18.59
233-3	1.0056	0.8201	81.08	18.92
233-4	1.0411	0.8494	81.12	18.88
233-5	0.9986	0.8143	81.07	18.93
		average	**81.17**	**18.83**
		confidence limit	**0.17**	**0.17**
		SD	**0.14**	**0.14**
		RSD %	**0.17**	**0.74**

- ***Influence of sample size***

0.500 g, 100 ml

JRC code	sample mass g	residue mass g	insoluble %	soluble %
199-1	0.5212	0.3415	64.82	35.18
199-2	0.5092	0.3317	64.43	35.57
199-3	0.5175	0.3383	64.67	35.33
		average	**64.64**	**35.36**
		confidence limit	**0.48**	**0.48**
		SD	**0.19**	**0.19**
		RSD %	**0.30**	**0.55**

0.250 g, 50 ml

JRC code	sample mass g	residue mass g	insoluble %	soluble %
199-1	0.2715	0.1774	64.63	35.37
199-2	0.2753	0.1791	64.35	35.65
199-3	0.2709	0.1765	64.44	35.56
		average	**64.48**	**35.52**
		confidence limit	**0.36**	**0.36**
		SD	**0.15**	**0.15**
		RSD %	**0.23**	**0.41**

0.200 g, 40 ml

JRC code	sample mass g	residue mass g	insoluble %	soluble %
199-1	0.2073	0.1350	64.41	35.59
199-2	0.2081	0.1355	64.40	35.60
199-3	0.2056	0.1339	64.42	35.58
		average	**64.41**	**35.59**
		confidence limit	**0.02**	**0.02**
		SD	**0.01**	**0.01**
		RSD %	**0.01**	**0.02**

0.150 g, 30 ml

JRC code	sample mass g	residue mass g	insoluble %	soluble %
199-1	0.1533	0.0976	62.94	37.06
199-2	0.1501	0.0967	63.71	36.29
199-3	0.1497	0.0966	63.81	36.19
		average	**63.49**	**36.51**
		confidence limit	**1.18**	**1.18**
		SD	**0.47**	**0.47**
		RSD %	**0.75**	**1.30**

0.100 g, 20 ml

JRC code	sample mass g	residue mass g	insoluble %	soluble %
199-1	0.1056	0.0684	64.06	35.94
199-2	0.1149	0.0744	64.04	35.96
199-3	0.1161	0.0751	63.97	36.03
		average	**64.02**	**35.98**
		confidence limit	**0.11**	**0.11**
		SD	**0.05**	**0.05**
		RSD %	**0.07**	**0.13**

0.100 g, 50 ml

JRC code	sample mass g	residue mass g	insoluble %	soluble %
199-1	0.1205	0.0774	63.52	36.48
199-2	0.1250	0.0805	63.68	36.32
199-3	0.1234	0.0795	63.71	36.29
199-4	0.1173	0.0755	63.65	36.35
199-5	0.1229	0.0790	63.56	36.44
199-6	0.1207	0.0775	63.49	36.51
199-7	0.1230	0.0790	63.51	36.49
199-8	0.1163	0.0749	63.69	36.31
199-9	0.1161	0.0748	63.71	36.29
		average	**63.61**	**36.39**
		confidence limit	**0.07**	**0.07**
		SD	**0.09**	**0.09**
		RSD %	**0.15**	**0.25**

0.250 g, 50 ml, light glassware

JRC code	sample mass g	residue mass g	insoluble %	soluble %
199-1	0.2504	0.1640	64.79	35.21
199-2	0.2505	0.1644	64.92	35.08
199-3	0.2491	0.1633	64.85	35.15
199-4	0.2456	0.1610	64.85	35.15
199-5	0.2472	0.1618	64.75	35.25
199-6	0.2574	0.1688	64.87	35.13
199-7	0.2546	0.1666	64.73	35.27
199-8	0.2447	0.1603	64.80	35.20
199-9	0.2497	0.1636	64.81	35.19
		average	**64.82**	**35.18**
		confidence limit	**0.05**	**0.05**
		SD	**0.06**	**0.06**
		RSD %	**0.09**	**0.17**

0.100 g, 50 ml, light glassware

JRC code	sample mass g	residue mass g	insoluble %	soluble %
199-1	0.1047	0.0685	64.72	35.28
199-2	0.1038	0.0678	64.61	35.39
199-3	0.1038	0.0678	64.61	35.39
199-4	0.1023	0.0670	64.79	35.21
199-5	0.1013	0.0662	64.64	35.36
199-6	0.1026	0.0670	64.59	35.41
199-7	0.1039	0.0679	64.64	35.36
199-8	0.1044	0.0681	64.52	35.48
199-9	0.1029	0.0672	64.60	35.40
199-10	0.1012	0.0661	64.61	35.39
		average	**64.63**	**35.37**
		confidence limit	**0.05**	**0.05**
		SD	**0.07**	**0.07**
		RSD %	**0.11**	**0.21**

- ***Combination with densitometry***

0.150 g, 50 ml, light glassware

JRC code	sample mass g	residue mass g	insoluble %	soluble %
255*-1	0.1515	0.1110	72.65	27.35
255*-2	0.1510	0.1101	72.30	27.70
255*-3	0.1518	0.1109	72.44	27.56
255*-4	0.1538	0.1125	72.53	27.47
255*-5	0.1498	0.1095	72.48	27.52
		average	**72.48**	**27.52**
		confidence limit	**0.16**	**0.16**
		SD	**0.13**	**0.13**
		RSD %	**0.18**	**0.48**

Chemical methods using formic acid solutions

PAC 5 %– 40 % (samples 195 - 199)

- ***Method B (98-100 % HCOOH, 3h, RT)***

JRC code	sample mass g	residue mass g	insoluble %	soluble %
195-1	1.0821	1.0556	97.48	2.52
195-2	1.0866	1.0578	97.27	2.73
195-3	1.0750	1.0463	97.25	2.75
195-4	1.0406	1.0273	98.68	1.32
195-5	1.0654	1.0465	98.17	1.83
195-6	1.0633	1.0406	97.80	2.20
195-7	1.0757	1.0548	98.00	2.00
195-8	1.0741	1.0519	97.87	2.13
		average	**97.81**	**2.19**
		confidence limit	**0.41**	**0.41**
		SD	**0.49**	**0.49**
		RSD %	**0.50**	**22.21**

JRC code	sample mass g	residue mass g	insoluble %	soluble %
196-1	1.0340	0.9455	91.19	8.81
196-2	1.0460	0.9524	90.80	9.20
196-3	1.0558	0.9669	91.34	8.66
		average	**91.11**	**8.89**
		confidence limit	**0.70**	**0.70**
		SD	**0.28**	**0.28**
		RSD %	**0.31**	**3.16**

JRC code	sample mass g	residue mass g	insoluble %	soluble %
197-1	1.0967	0.9034	81.92	18.08
197-2	1.0544	0.8693	81.99	18.01
197-3	1.0201	0.8344	81.33	18.67
197-4	1.0494	0.8612	81.60	18.40
197-5	1.0556	0.8683	81.80	18.20
		average	**81.73**	**18.27**
		confidence limit	**0.33**	**0.33**
		SD	**0.27**	**0.27**
		RSD %	**0.33**	**1.46**

JRC code	sample mass g	residue mass g	insoluble %	soluble %
198-1	1.0447	0.7728	73.37	26.63
198-2	1.0424	0.7631	72.59	27.41
198-3	1.0454	0.7683	72.88	27.12
198-4	1.0076	0.7391	72.74	27.26
198-5	1.0047	0.7335	72.39	27.61
		average	**72.80**	**27.20**
		confidence limit	**0.46**	**0.46**
		SD	**0.37**	**0.37**
		RSD %	**0.51**	**1.36**

JRC code	sample mass g	residue mass g	insoluble %	soluble %
199-1	1.0504	0.6940	65.37	34.63
199-2	1.0148	0.6694	65.26	34.74
		average	**65.32**	**34.68**
		confidence limit	**0.68**	**0.68**
		SD	**0.08**	**0.08**
		RSD %	**0.12**	**0.22**

- ## *Method C (98-100 % HCOOH, 15 min, RT)*

JRC code	sample mass g	residue mass g	insoluble %	soluble %
195-1	1.0387	1.0029	96.45	3.55
195-2	1.0315	1.0214	98.99	1.01
		average	**97.72**	**2.28**
		confidence limit	**16.15**	**16.15**
		SD	**1.80**	**1.80**
		RSD %	**1.84**	**78.81**

JRC code	sample mass g	residue mass g	insoluble %	soluble %
196-1	1.0558	1.0059	95.13	4.87
196-2	1.0242	0.9720	94.75	5.25
196-3	1.0115	0.9374	92.46	7.54
196-4	1.0635	1.0006	93.91	6.09
196-5	1.0583	1.0171	95.99	4.01
196-6	1.0251	0.9873	96.20	3.80
		average	**94.74**	**5.26**
		confidence limit	**1.46**	**1.46**
		SD	**1.40**	**1.40**
		RSD %	**1.47**	**26.53**

JRC code	sample mass g	residue mass g	insoluble %	soluble %
197-1	1.0162	0.8446	82.67	17.33
197-2	1.0322	0.8573	82.61	17.39
197-3	1.0509	0.8688	82.22	17.78
197-4	1.1493	0.9482	82.05	17.95
197-5	1.0673	0.8797	81.97	18.03
		average	**82.31**	**17.69**
		confidence limit	**0.40**	**0.40**
		SD	**0.32**	**0.32**
		RSD %	**0.39**	**1.82**

JRC code	sample mass g	residue mass g	insoluble %	soluble %
198-1	1.0451	0.7704	73.11	26.89
198-2	1.0404	0.7667	73.09	26.91
198-3	1.0835	0.7989	73.13	26.87
		average	**73.11**	**26.89**
		confidence limit	**0.05**	**0.05**
		SD	**0.02**	**0.02**
		RSD %	**0.03**	**0.08**

JRC code	sample mass g	residue mass g	insoluble %	soluble %
199-1	1.0338	0.6854	65.60	34.40
199-2	1.0189	0.6659	64.65	35.35
199-3	1.0280	0.6792	65.37	34.63
199-4	1.0341	0.6849	65.53	34.47
199-5	1.0247	0.6780	65.47	34.53
		average	**65.32**	**34.68**
		confidence limit	**0.48**	**0.48**
		SD	**0.39**	**0.39**
		RSD %	**0.59**	**1.12**

- ## Method D (80 % HCOOH, 7h, RT)

JRC code	sample mass g	residue mass g	insoluble %	soluble %
199-1	1.0003	0.6778	67.08	32.92
199-2	1.1303	0.7634	66.85	33.15
199-3	1.0904	0.7356	66.78	33.22
		average	**66.90**	**33.10**
		confidence limit	**0.39**	**0.39**
		SD	**0.16**	**0.16**
		RSD %	**0.23**	**0.47**

- ## Method E (80 % HCOOH, 1h, RT)

JRC code	sample mass g	residue mass g	insoluble %	soluble %
199-1	1.1527	0.7791	66.90	33.10
199-2	1.1116	0.7487	66.67	33.33
199-3	1.0627	0.7192	66.99	33.01
		average	**66.85**	**33.15**
		confidence limit	**0.42**	**0.42**
		SD	**0.17**	**0.17**
		RSD %	**0.25**	**0.51**

- ## Method F (80 % HCOOH, 15 min, RT) = method 4 of Dir. 96/73/EC

JRC code	sample mass g	residue mass g	insoluble %	soluble %
195-1	1.1895	1.1883	99.90	0.10
195-2	1.0478	1.0457	99.79	0.21
195-3	1.0329	1.0308	99.79	0.21
195-4	1.1165	1.1139	99.76	0.24
195-5	1.0750	1.0723	99.74	0.26
195-6	1.1390	1.1381	99.92	0.08
195-7	1.0099	1.0065	99.65	0.35
195-8	1.1443	1.1397	99.59	0.41
195-9	1.0327	1.0281	99.54	0.46
195-10	1.1690	1.1661	99.74	0.26
		average	**99.74**	**0.26**
		confidence limit	**0.09**	**0.09**
		SD	**0.12**	**0.12**
		RSD %	**0.12**	**47.18**

JRC code	sample mass g	residue mass g	insoluble %	soluble %
196-1	1.0841	1.0812	99.72	0.28
196-2	1.1229	1.1190	99.64	0.36
196-3	1.0925	1.0858	99.37	0.63
196-4	1.0669	1.0637	99.69	0.31
196-5	1.0419	1.0375	99.56	0.44
196-6	1.0780	1.0742	99.64	0.36
196-7	1.0191	1.0134	99.42	0.58
196-8	1.0679	1.0643	99.65	0.35
196-9	1.1671	1.1641	99.73	0.27
		average	**99.60**	**0.40**
		confidence limit	**0.10**	**0.10**
		SD	**0.13**	**0.13**
		RSD %	**0.13**	**32.68**

JRC code	sample mass g	residue mass g	insoluble %	soluble %
197-1	1.0177	1.0034	98.55	1.45
197-2	1.0104	1.0005	98.99	1.01
197-3	1.0048	0.9978	99.28	0.72
197-4	1.0169	1.0050	98.79	1.21
197-5	1.0438	1.0295	98.59	1.41
197-6	1.0497	1.0363	98.68	1.32
197-7	1.0164	1.0074	99.09	0.91
197-8	1.0083	0.9910	98.23	1.77
197-9	1.0120	0.9988	98.66	1.34
		average	**98.76**	**1.24**
		confidence limit	**0.24**	**0.24**
		SD	**0.32**	**0.32**
		RSD %	**0.32**	**25.59**

JRC code	sample mass g	residue mass g	insoluble %	soluble %
198-1	1.0469	0.8586	81.55	18.45
198-2	1.0050	0.8234	81.47	18.53
198-3	1.0452	0.8473	80.58	19.42
198-4	1.1101	0.8971	80.33	19.67
198-5	1.2036	0.9672	79.86	20.14
198-6	1.1931	0.9975	83.18	16.82
198-7	1.1996	1.0009	83.00	17.00
198-8	1.1645	0.9600	81.98	18.02
198-9	1.1230	0.9161	81.10	18.90
198-10	1.0261	0.8372	81.12	18.88
		average	**81.42**	**18.58**
		confidence limit	**0.77**	**0.77**
		SD	**1.08**	**1.08**
		RSD %	**1.32**	**5.79**

JRC code	sample mass g	residue mass g	insoluble %	soluble %
199-1	1.079	0.7298	66.95	33.05
199-2	1.0825	0.7293	66.69	33.31
199-3	1.0691	0.7191	66.57	33.43
199-4	1.0637	0.7158	66.61	33.39
199-5	1.0511	0.7103	66.89	33.11
199-6	1.0244	0.6944	67.10	32.90
199-7	1.0361	0.7049	67.35	32.65
199-8	0.9972	0.6781	67.32	32.68
199-9	1.0566	0.7131	66.80	33.20
199-10	1.0779	0.7313	67.16	32.84
199-11	1.0283	0.6968	67.08	32.92
199-12	1.2898	0.8762	67.25	32.75
199-13	1.102	0.7438	66.81	33.19
199-14	1.1711	0.7947	67.18	32.82
		average	**66.98**	**33.02**
		confidence limit	**0.15**	**0.15**
		SD	**0.26**	**0.26**
		RSD %	**0.39**	**0.79**

Method 13 of Directive 96/73/EC

PAC 5 % – 40 % (samples 195 - 199)

JRC code	sample mass g	residue mass g	insoluble %	soluble %
195-1	1.0162	0.0505	5.12	94.88
195-2	1.0053	0.0484	4.96	95.04
195-3	0.9999	0.0485	5.00	95.00
195-4	1.0187	0.0539	5.45	94.55
195-5	1.0550	0.0516	5.04	94.96
		average	**5.11**	**94.89**
		confidence limit	**0.25**	**0.25**
		SD	**0.20**	**0.20**
		RSD %	**3.86**	**0.21**

JRC code	sample mass g	residue mass g	insoluble %	soluble %
196-1	1.0309	0.1110	11.07	88.93
196-2	1.0167	0.1108	11.20	88.80
196-3	1.0243	0.1157	11.61	88.39
196-4	1.0061	0.1133	11.58	88.42
196-5	1.0079	0.1078	11.00	89.00
		average	**11.29**	**88.71**
		confidence limit	**0.35**	**0.35**
		SD	**0.29**	**0.29**
		RSD %	**2.53**	**0.32**

JRC code	sample mass g	residue mass g	insoluble %	soluble %
197-1	1.0523	0.2093	20.39	79.61
197-2	1.0219	0.1945	19.52	80.48
197-3	1.0340	0.2060	20.42	79.58
197-4	1.0219	0.1946	19.53	80.47
197-5	1.0125	0.2009	20.34	79.66
		average	**20.04**	**79.96**
		confidence limit	**0.59**	**0.59**
		SD	**0.47**	**0.47**
		RSD %	**2.36**	**0.59**

JRC code	sample mass g	residue mass g	insoluble %	soluble %
198-1	1.0103	0.2948	29.83	70.17
198-2	1.0106	0.2984	30.18	69.82
198-3	1.0290	0.3037	30.16	69.84
198-4	1.0292	0.3018	29.97	70.03
198-5	1.0449	0.3047	29.81	70.19
		average	**29.99**	**70.01**
		confidence limit	**0.22**	**0.22**
		SD	**0.18**	**0.18**
		RSD %	**0.59**	**0.25**

JRC code	sample mass g	residue mass g	insoluble %	soluble %
199-1	1.053	0.4145	40.11	59.89
199-2	0.9973	0.3968	40.53	59.47
199-3	1.0389	0.41034	40.24	59.76
199-4	1.2188	0.4783	39.99	60.01
199-5	1.0133	0.4006	40.28	59.72
199-6	1.0329	0.4065	40.10	59.90
199-7	1.0126	0.4042	40.66	59.34
199-8	1.0413	0.4071	39.84	60.16
		average	**40.22**	**59.78**
		confidence limit	**0.23**	**0.23**
		SD	**0.27**	**0.27**
		RSD %	**0.68**	**0.46**

Manual separation

Binary mixtures PA6/PAC (samples 201, 203, 205, 206)

JRC code	PAC mass g	PA6 mass g	sample mass g	PAC %	PA6 %
201-1	0.6712	0.7456	1.4168	46.23	53.77
201-2	0.5990	0.6574	1.2564	46.53	53.47
201-3	0.5208	0.5916	1.1124	45.68	54.32
201-4	0.5819	0.6557	1.2376	45.88	54.12
201-5	0.5471	0.6169	1.1640	45.86	54.14
201-6	0.5551	0.6313	1.1864	45.65	54.35
201-7	0.5599	0.6320	1.1919	45.83	54.17
201-8	0.5678	0.6145	1.1823	46.88	53.12
201-9	0.5833	0.6562	1.2395	45.92	54.08
201-10	0.5993	0.6768	1.2761	45.82	54.18
			average	**46.03**	**53.97**
			confidence limit	**0.29**	**0.29**
			SD	**0.40**	**0.40**
			RSD %	**0.87**	**0.74**

JRC code	PAC mass g	PA6 mass g	sample mass g	PAC %	PA6 %
203-1	0.5432	0.5983	1.1415	46.44	53.56
203-2	0.5787	0.6511	1.2298	45.91	54.09
203-3	0.5828	0.6264	1.2092	47.05	52.95
203-4	0.6100	0.6626	1.2726	46.79	53.21
203-5	0.6116	0.6546	1.2662	47.16	52.84
203-6	0.5275	0.6005	1.1280	45.62	54.38
203-7	0.5748	0.6343	1.2091	46.39	53.61
203-8	0.5737	0.6539	1.2276	45.59	54.41
203-9	0.4955	0.5609	1.0564	45.76	54.24
203-10	0.5712	0.6162	1.1874	46.96	53.04
			average	**46.37**	**53.63**
			confidence limit	**0.44**	**0.44**
			SD	**0.61**	**0.61**
			RSD %	**1.32**	**1.14**

JRC code	PAC mass g	PA6 mass g	sample mass g	PAC %	PA6 %
205-1	0.5175	0.5598	1.0773	46.89	53.11
205-2	0.5858	0.6226	1.2084	47.33	52.67
205-3	0.5565	0.582	1.1385	47.73	52.27
205-4	0.5997	0.6373	1.2370	47.33	52.67
205-5	0.5482	0.5786	1.1268	47.50	52.50
205-6	0.5061	0.5593	1.0654	46.36	53.64
205-7	0.6276	0.6864	1.3140	46.62	53.38
205-8	0.5715	0.6193	1.1908	46.85	53.15
205-9	0.5325	0.6023	1.1348	45.78	54.22
205-10	0.5211	0.5915	1.1126	45.69	54.31
			average	**46.81**	**53.19**
			confidence limit	**0.50**	**0.50**
			SD	**0.70**	**0.70**
			RSD %	**1.50**	**1.32**

JRC code	PAC mass g	PA6 mass g	sample mass g	PAC %	PA6 %
206-1	0.5341	0.5765	1.1106	46.95	53.05
206-2	0.5683	0.6409	1.2092	45.86	54.14
206-3	0.5467	0.6018	1.1485	46.46	53.54
206-4	0.6076	0.6384	1.2460	47.62	52.38
206-5	0.5077	0.5429	1.0506	47.18	52.82
206-6	0.5827	0.6403	1.2230	46.50	53.50
206-7	0.4620	0.5165	0.9785	46.07	53.93
206-8	0.4467	0.5171	0.9638	45.21	54.79
206-9	0.4304	0.4757	0.9061	46.36	53.64
			average	**46.47**	**53.53**
			confidence limit	**0.56**	**0.56**
			SD	**0.72**	**0.72**
			RSD %	**1.56**	**1.35**

Binary mixtures PP/PAC (samples 208, 210, 212, 213)

JRC code	PAC mass g	PP mass g	sample mass g	PAC %	PP %
208-1	0.6028	0.6061	1.2089	49.37	50.63
208-2	0.5939	0.6121	1.2060	48.76	51.24
208-3	0.5437	0.5482	1.0919	49.30	50.70
208-4	0.5417	0.545	1.0867	49.36	50.64
208-5	0.5994	0.6013	1.2007	49.43	50.57
208-6	0.509	0.5138	1.0228	49.28	50.72
208-7	0.6024	0.5921	1.1945	49.94	50.06
208-8	0.6194	0.5915	1.2109	50.66	49.34
208-9	0.4866	0.4782	0.9648	49.95	50.05
208-10	0.5418	0.5546	1.0964	48.93	51.07
			average	**49.50**	**50.50**
			confidence limit	**0.40**	**0.40**
			SD	**0.55**	**0.55**
			RSD %	**1.12**	**1.10**

JRC code	PAC mass g	PP mass g	sample mass g	PAC %	PP %
210-1	0.5822	0.561	1.1432	50.44	49.56
210-2	0.5703	0.569	1.1393	49.57	50.43
210-3	0.5597	0.5621	1.1218	49.40	50.60
210-4	0.5737	0.5701	1.1438	49.67	50.33
210-5	0.5638	0.5658	1.1296	49.42	50.58
210-6	0.5594	0.5525	1.1119	49.82	50.18
210-7	0.5772	0.5718	1.1490	49.74	50.26
210-8	0.5804	0.5565	1.1369	50.56	49.44
210-9	0.5542	0.5621	1.1163	49.16	50.84
210-10	0.5965	0.5951	1.1916	49.57	50.43
			average	**49.73**	**50.27**
			confidence limit	**0.32**	**0.32**
			SD	**0.45**	**0.45**
			RSD %	**0.90**	**0.89**

JRC code	PAC mass g	PP mass g	sample mass g	PAC %	PP %
212-1	0.5510	0.5431	1.0941	49.87	50.13
212-2	0.5854	0.5617	1.1471	50.54	49.46
212-3	0.5475	0.5514	1.0989	49.33	50.67
212-4	0.5777	0.5503	1.128	50.72	49.28
212-5	0.5123	0.4816	0.9939	51.05	48.95
212-6	0.5341	0.5342	1.0683	49.51	50.49
212-7	0.5636	0.5678	1.1314	49.32	50.68
212-8	0.5745	0.5763	1.1508	49.43	50.57
212-9	0.5620	0.5650	1.127	49.38	50.62
212-10	0.5442	0.5428	1.087	49.57	50.43
			average	**49.87**	**50.13**
			confidence limit	**0.47**	**0.47**
			SD	**0.65**	**0.65**
			RSD %	**1.31**	**1.30**

JRC code	PAC mass g	PP mass g	sample mass g	PAC %	PP %
213-1	0.6866	0.6437	1.3303	51.12	48.88
213-2	0.6946	0.6700	1.3646	50.41	49.59
213-3	0.7065	0.7123	1.4188	49.31	50.69
213-4	0.6622	0.6295	1.2917	50.78	49.22
213-5	0.8036	0.7798	1.5834	50.26	49.74
213-6	0.6291	0.6281	1.2572	49.55	50.45
213-7	0.6964	0.6608	1.3572	50.82	49.18
213-8	0.7253	0.6673	1.3926	51.59	48.41
213-9	0.6956	0.6667	1.3623	50.57	49.43
213-10	0.6962	0.6789	1.3751	50.14	49.86
			average	**50.45**	**49.55**
			confidence limit	**0.49**	**0.49**
			SD	**0.69**	**0.69**
			RSD %	**1.37**	**1.39**

Carpet samples PA6/PAC (samples 234 - 239)

JRC code	PAC mass g	PA6 mass g	sample mass g	PAC %	PA6 %
234-1	0.5638	0.5977	1.1615	47.39	52.61
234-2	0.5618	0.5878	1.1496	47.72	52.28
234-3	0.5490	0.5824	1.1314	47.38	52.62
234-4	0.5758	0.6081	1.1839	47.49	52.51
234-5	0.6303	0.6425	1.2728	48.37	51.63
234-6	0.5554	0.5561	1.1115	48.82	51.18
234-7	0.5611	0.5974	1.1585	47.29	52.71
234-8	0.5530	0.5852	1.1382	47.44	52.56
234-9	0.5683	0.5883	1.1566	47.99	52.01
234-10	0.5691	0.5993	1.1684	47.56	52.44
			average	**47.74**	**52.26**
			confidence limit	**0.36**	**0.36**
			SD	**0.50**	**0.50**
			RSD %	**1.05**	**0.96**

JRC code	PAC mass g	PA6 mass g	sample mass g	PAC %	PA6 %
235-1	0.5560	0.5969	1.1529	47.08	52.92
235-2	0.5544	0.5925	1.1469	47.19	52.81
235-3	0.5223	0.5845	1.1068	46.05	53.95
235-4	0.5435	0.6076	1.1511	46.07	53.93
235-5	0.5440	0.6078	1.1518	46.09	53.91
235-6	0.5355	0.5806	1.1161	46.83	53.17
235-7	0.5478	0.6006	1.1484	46.56	53.44
235-8	0.5490	0.5992	1.1482	46.67	53.33
235-9	0.5558	0.6091	1.1649	46.57	53.43
235-10	0.5517	0.6126	1.1643	46.24	53.76
			average	**46.53**	**53.47**
			confidence limit	**0.30**	**0.30**
			SD	**0.42**	**0.42**
			RSD %	**0.90**	**0.78**

JRC code	PAC mass g	PA6 mass g	sample mass g	PAC %	PA6 %
236-1	0.5638	0.6215	1.1853	46.42	53.58
236-2	0.5342	0.5839	1.1181	46.63	53.37
236-3	0.5573	0.5995	1.1568	47.03	52.97
236-4	0.5414	0.5940	1.1354	46.54	53.46
236-5	0.4992	0.5551	1.0543	46.20	53.80
236-6	0.5715	0.6322	1.2037	46.33	53.67
236-7	0.5135	0.5925	1.1060	45.29	54.71
236-8	0.5383	0.5953	1.1336	46.34	53.66
236-9	0.5336	0.6004	1.1340	45.91	54.09
236-10	0.5510	0.5990	1.1500	46.77	53.23
			average	**46.35**	**53.65**
			confidence limit	**0.35**	**0.35**
			SD	**0.48**	**0.48**
			RSD %	**1.04**	**0.90**

JRC code	PAC mass g	PA6 mass g	sample mass g	PAC %	PA6 %
237-1	0.5723	0.6118	1.1841	47.19	52.81
237-2	0.5305	0.5786	1.1091	46.69	53.31
237-3	0.5068	0.5785	1.0853	45.55	54.45
237-4	0.5640	0.6067	1.1707	47.03	52.97
237-5	0.5484	0.6031	1.1515	46.48	53.52
237-6	0.5310	0.5923	1.1233	46.13	53.87
237-7	0.5383	0.5891	1.1274	46.60	53.40
237-8	0.5374	0.5867	1.1241	46.66	53.34
237-9	0.5517	0.5816	1.1333	47.53	52.47
237-10	0.5410	0.5886	1.1296	46.75	53.25
			average	**46.66**	**53.34**
			confidence limit	**0.39**	**0.39**
			SD	**0.55**	**0.55**
			RSD %	**1.18**	**1.03**

JRC code	PAC mass g	PA6 mass g	sample mass g	PAC %	PA6 %
238-1	0.5439	0.5928	1.1367	46.70	53.30
238-2	0.5527	0.5960	1.1487	46.97	53.03
238-3	0.5390	0.5992	1.1382	46.21	53.79
238-4	0.5237	0.5836	1.1073	46.15	53.85
238-5	0.5187	0.5904	1.1091	45.63	54.37
238-6	0.5170	0.5900	1.1070	45.56	54.44
238-7	0.5548	0.5953	1.1501	47.09	52.91
238-8	0.5320	0.5794	1.1114	46.72	53.28
238-9	0.5558	0.5892	1.1450	47.39	52.61
238-10	0.5493	0.5930	1.1423	46.94	53.06
			average	**46.54**	**53.46**
			confidence limit	**0.45**	**0.45**
			SD	**0.62**	**0.62**
			RSD %	**1.34**	**1.17**

JRC code	PAC mass g	PA6 mass g	sample mass g	PAC %	PA6 %
239-1	0.5523	0.5843	1.1366	47.45	52.55
239-2	0.5467	0.5823	1.129	47.28	52.72
239-3	0.5163	0.5791	1.0954	45.99	54.01
239-4	0.5305	0.584	1.1145	46.45	53.55
239-5	0.551	0.5909	1.1419	47.11	52.89
239-6	0.5177	0.5804	1.0981	46.00	54.00
239-7	0.5465	0.5980	1.1445	46.60	53.40
239-8	0.5563	0.5954	1.1517	47.16	52.84
239-9	0.533	0.607	1.14	45.61	54.39
239-10	0.5057	0.5815	1.0872	45.37	54.63
			average	**46.50**	**53.50**
			confidence limit	**0.53**	**0.53**
			SD	**0.74**	**0.74**
			RSD %	**1.58**	**1.38**

Carpet samples PP/PAC (samples 246 - 254)

JRC code	PAC mass g	PP mass g	sample mass g	PAC %	PP %
246-1	0.5634	0.4173	0.9807	56.97	43.03
246-2	0.5420	0.4127	0.9547	56.29	43.71
246-3	0.5456	0.4175	0.9631	56.17	43.83
246-4	0.5564	0.4225	0.9789	56.36	43.64
246-5	0.5576	0.4086	0.9662	57.23	42.77
246-6	0.5511	0.4112	0.9623	56.79	43.21
246-7	0.5667	0.4079	0.9746	57.67	42.33
246-8	0.5432	0.4169	0.9601	56.10	43.90
246-9	0.5557	0.4185	0.9742	56.56	43.44
246-10	0.5578	0.4245	0.9823	56.30	43.70
			average	**56.64**	**43.36**
			confidence limit	**0.37**	**0.37**
			SD	**0.51**	**0.51**
			RSD %	**0.91**	**1.19**

JRC code	PAC mass g	PP mass g	sample mass g	PAC %	PP %
247-1	0.5442	0.4004	0.9446	57.13	42.87
247-2	0.5521	0.4147	0.9668	56.62	43.38
247-3	0.5504	0.4018	0.9522	57.32	42.68
247-4	0.5626	0.4043	0.9669	57.71	42.29
247-5	0.5707	0.4129	0.9836	57.54	42.46
247-6	0.5277	0.3903	0.9180	57.00	43.00
247-7	0.5296	0.4017	0.9313	56.39	43.61
247-8	0.5488	0.4258	0.9746	55.83	44.17
247-9	0.4896	0.3755	0.8651	56.11	43.89
247-10	0.6319	0.4542	1.0861	57.70	42.30
			average	**56.94**	**43.06**
			confidence limit	**0.48**	**0.48**
			SD	**0.67**	**0.67**
			RSD %	**1.18**	**1.56**

JRC code	PAC mass g	PP mass g	sample mass g	PAC %	PP %
248-1	0.5459	0.4055	0.9514	56.90	43.10
248-2	0.5449	0.4072	0.9521	56.75	43.25
248-3	0.5434	0.413	0.9564	56.34	43.66
248-4	0.5102	0.3879	0.8981	56.33	43.67
248-5	0.5701	0.4273	0.9974	56.68	43.32
248-6	0.5269	0.4002	0.9271	56.35	43.65
248-7	0.5239	0.3991	0.9230	56.28	43.72
248-8	0.5534	0.4121	0.9655	56.84	43.16
248-9	0.5355	0.4026	0.9381	56.60	43.40
248-10	0.532	0.4055	0.9375	56.26	43.74
			average	**56.53**	**43.47**
			confidence limit	**0.18**	**0.18**
			SD	**0.25**	**0.25**
			RSD %	**0.44**	**0.57**

JRC code	PAC mass g	PP mass g	sample mass g	PAC %	PP %
249-1	0.5416	0.4018	0.9434	56.93	43.07
249-2	0.5391	0.4200	0.9591	55.73	44.27
249-3	0.5260	0.4012	0.9272	56.25	43.75
249-4	0.5565	0.4101	0.9666	57.09	42.91
249-5	0.5407	0.3996	0.9403	57.02	42.98
249-6	0.5174	0.3950	0.9124	56.23	43.77
249-7	0.5280	0.4030	0.9310	56.23	43.77
249-8	0.5165	0.3996	0.9161	55.90	44.10
249-9	0.5090	0.3900	0.8990	56.14	43.86
249-10	0.5222	0.4001	0.9223	56.14	43.86
			average	**56.36**	**43.64**
			confidence limit	**0.34**	**0.34**
			SD	**0.48**	**0.48**
			RSD %	**0.85**	**1.10**

JRC code	PAC mass g	PP mass g	sample mass g	PAC %	PP %
250-1	0.5145	0.3748	0.8893	57.38	42.62
250-2	0.5454	0.4150	0.9604	56.31	43.69
250-3	0.5401	0.4115	0.9516	56.28	43.72
250-4	0.4894	0.3796	0.8690	55.83	44.17
250-5	0.5319	0.3999	0.9318	56.60	43.40
250-6	0.5144	0.3874	0.9018	56.56	43.44
250-7	0.5226	0.4009	0.9235	56.11	43.89
250-8	0.5229	0.4018	0.9247	56.07	43.93
250-9	0.5258	0.4105	0.9363	55.67	44.33
250-10	0.5145	0.4037	0.9182	55.55	44.45
			average	**56.24**	**43.76**
			confidence limit	**0.38**	**0.38**
			SD	**0.53**	**0.53**
			RSD %	**0.94**	**1.21**

JRC code	PAC mass g	PP mass g	sample mass g	PAC %	PP %
251-1	0.5153	0.4113	0.9266	55.13	44.87
251-2	0.5113	0.4050	0.9163	55.32	44.68
251-3	0.5152	0.4116	0.9268	55.10	44.90
251-4	0.5011	0.3974	0.8985	55.29	44.71
251-5	0.5587	0.4118	0.9705	57.09	42.91
251-6	0.5421	0.3985	0.9406	57.15	42.85
251-7	0.5187	0.3966	0.9153	56.19	43.81
251-8	0.5074	0.3917	0.8991	55.95	44.05
251-9	0.5148	0.4166	0.9314	54.79	45.21
251-10	0.4992	0.3974	0.8966	55.19	44.81
			average	**55.72**	**44.28**
			confidence limit	**0.60**	**0.60**
			SD	**0.85**	**0.85**
			RSD %	**1.52**	**1.91**

JRC code	PAC mass g	PP mass g	sample mass g	PAC %	PP %
252-1	0.6028	0.4624	1.0652	56.11	43.89
252-2	0.6489	0.4867	1.1356	56.66	43.34
252-3	0.6612	0.4993	1.1605	56.49	43.51
252-4	0.6562	0.4965	1.1527	56.45	43.55
252-5	0.6568	0.499	1.1558	56.34	43.66
252-6	0.6571	0.4962	1.1533	56.49	43.51
252-7	0.6587	0.4985	1.1572	56.44	43.56
252-8	0.6402	0.487	1.1272	56.31	43.69
			average	**56.41**	**43.59**
			confidence limit	**0.14**	**0.14**
			SD	**0.16**	**0.16**
			RSD %	**0.29**	**0.37**

JRC code	PAC mass g	PP mass g	sample mass g	PAC %	PP %
253-1	0.6027	0.4585	1.0612	56.31	43.69
253-2	0.6098	0.4560	1.0658	56.73	43.27
253-3	0.6541	0.4927	1.1468	56.56	43.44
253-4	0.6498	0.4982	1.1480	56.12	43.88
253-5	0.6576	0.4864	1.1440	57.00	43.00
253-6	0.6478	0.5036	1.1514	55.78	44.22
253-7	0.6545	0.4963	1.1508	56.39	43.61
253-8	0.6546	0.4951	1.1497	56.46	43.54
			average	**56.42**	**43.58**
			confidence limit	**0.31**	**0.31**
			SD	**0.37**	**0.37**
			RSD %	**0.66**	**0.85**

JRC code	PAC mass g	PP mass g	sample mass g	PAC %	PP %
254-1	0.6044	0.4611	1.0655	56.24	43.76
254-2	0.5574	0.4263	0.9837	56.18	43.82
254-3	0.6523	0.4992	1.1515	56.17	43.83
254-4	0.6006	0.4562	1.0568	56.35	43.65
254-5	0.5994	0.4607	1.0601	56.06	43.94
254-6	0.6504	0.4972	1.1476	56.19	43.81
254-7	0.6028	0.4639	1.0667	56.03	43.97
254-8	0.6541	0.5047	1.1588	55.96	44.04
			average	**56.15**	**43.85**
			confidence limit	**0.10**	**0.10**
			SD	**0.13**	**0.13**
			RSD %	**0.22**	**0.29**

Quantification of binary mixtures and carpet samples

Method 11 of Directive 96/73/EC

Binary mixtures PA6/PAC (samples 200 – 206)

JRC code	sample mass g	residue mass g	PAC %	PA6 %
200-1	1.0072	0.4769	46.68	53.32
200-2	1.0639	0.5108	47.35	52.65
200-3	1.0715	0.5135	47.26	52.74
200-4	1.0286	0.4903	47.00	53.00
200-5	1.0442	0.4989	47.11	52.89
200-6	1.0559	0.4979	46.48	53.52
200-7	1.0610	0.5017	46.61	53.39
200-8	1.0557	0.5008	46.77	53.23
200-9	1.0780	0.5095	46.59	53.41
		average	**46.87**	**53.13**
		confidence limit	**0.24**	**0.24**
		SD	**0.31**	**0.31**
		RSD %	**0.67**	**0.59**

JRC code	sample mass g	residue mass g	PAC %	PA6 %
201-1	1.0615	0.4968	46.13	53.87
201-2	1.0050	0.4645	45.54	54.46
201-3	1.1129	0.5281	46.78	53.22
201-4	1.0125	0.4689	45.63	54.37
201-5	1.0646	0.4979	46.09	53.91
201-6	1.0737	0.5091	46.74	53.26
201-7	1.0735	0.5009	45.98	54.02
201-8	1.0462	0.4891	46.07	53.93
201-9	1.0731	0.5014	46.05	53.95
201-10	1.0299	0.4865	46.56	53.44
		average	**46.16**	**53.84**
		confidence limit	**0.30**	**0.30**
		SD	**0.42**	**0.42**
		RSD %	**0.92**	**0.79**

JRC code	sample mass g	residue mass g	PAC %	PA6 %
202-1	1.0675	0.5219	48.23	51.77
202-2	1.0434	0.5109	48.31	51.69
202-3	0.9979	0.4777	47.20	52.80
202-4	1.0219	0.4977	48.04	51.96
202-5	1.0002	0.4904	48.37	51.63
202-6	1.0384	0.4994	47.43	52.57
202-7	1.0361	0.5006	47.65	52.35
202-8	1.0754	0.5199	47.68	52.32
202-9	1.0583	0.5050	47.05	52.95
202-10	1.0387	0.5034	47.80	52.20
		average	**47.78**	**52.22**
		confidence limit	**0.33**	**0.33**
		SD	**0.46**	**0.46**
		RSD %	**0.97**	**0.88**

JRC code	sample mass g	residue mass g	PAC %	PA6 %
203-1	1.0639	0.5122	47.48	52.52
203-2	1.0194	0.4877	47.17	52.83
203-3	1.0054	0.4846	47.53	52.47
203-4	1.0057	0.4834	47.40	52.60
203-5	1.2997	0.6163	46.75	53.25
203-6	1.0196	0.4898	47.37	52.63
203-7	1.0192	0.4889	47.30	52.70
203-8	1.0034	0.4780	46.97	53.03
203-9	1.0270	0.4874	46.79	53.21
203-10	1.0700	0.5070	46.71	53.29
		average	**47.15**	**52.85**
		confidence limit	**0.23**	**0.23**
		SD	**0.32**	**0.32**
		RSD %	**0.67**	**0.60**

JRC code	sample mass g	residue mass g	PAC %	PA6 %
204-1	1.0088	0.4877	47.68	52.32
204-2	1.0761	0.5055	46.30	53.70
204-3	1.0439	0.4985	47.08	52.92
204-4	1.1052	0.5294	47.23	52.77
204-5	1.0796	0.4997	45.61	54.39
204-6	1.0290	0.4975	47.68	52.32
204-7	1.0769	0.5112	46.80	53.20
204-8	1.0161	0.4834	46.90	53.10
204-9	1.0700	0.5194	47.88	52.12
204-10	1.0271	0.5178	49.77	50.23
		average	**47.29**	**52.71**
		confidence limit	**0.79**	**0.79**
		SD	**1.11**	**1.11**
		RSD %	**2.34**	**2.10**

JRC code	sample mass g	residue mass g	PAC %	PA6 %
205-1	1.0080	0.4807	47.02	52.98
205-2	1.0202	0.4906	47.42	52.58
205-3	1.0192	0.4855	46.97	53.03
205-4	1.0240	0.4937	47.55	52.45
205-5	1.0053	0.4753	46.61	53.39
205-6	1.0088	0.4843	47.34	52.66
205-7	1.0314	0.5009	47.90	52.10
205-8	1.0165	0.4888	47.42	52.58
205-9	1.0735	0.5161	47.41	52.59
205-10	1.0584	0.5060	47.14	52.86
		average	**47.28**	**52.72**
		confidence limit	**0.26**	**0.26**
		SD	**0.36**	**0.36**
		RSD %	**0.76**	**0.68**

JRC code	sample mass g	residue mass g	PAC %	PA6 %
206-1	1.0180	0.4843	46.90	53.10
206-2	1.0302	0.4943	47.31	52.69
206-3	1.0061	0.4849	47.53	52.47
206-4	1.0254	0.5042	48.51	51.49
206-5	1.0664	0.5103	47.18	52.82
206-6	1.0280	0.4675	44.79	55.21
206-7	1.0361	0.4920	46.81	53.19
206-8	1.0325	0.5149	49.22	50.78
206-9	1.0150	0.4530	43.94	56.06
		average	**46.91**	**53.09**
		confidence limit	**1.27**	**1.27**
		SD	**1.65**	**1.65**
		RSD %	**3.52**	**3.11**

Carpet samples PA6/PAC (samples 234 – 239)

JRC code	sample mass g	residue mass g	PAC %	PA6 %
234-1	1.1592	0.5578	47.45	52.55
234-2	1.1489	0.5563	47.76	52.24
234-3	1.1291	0.5432	47.44	52.56
234-4	1.1807	0.5699	47.60	52.40
234-5	1.2700	0.6236	48.44	51.56
		average	**47.74**	**52.26**
		confidence limit	**0.51**	**0.51**
		SD	**0.41**	**0.41**
		RSD %	**0.87**	**0.79**

JRC code	sample mass g	residue mass g	PAC %	PA6 %
235-1	1.1518	0.5523	47.28	52.72
235-2	1.1446	0.5506	47.44	52.56
235-3	1.1060	0.5226	46.58	53.42
235-4	1.1496	0.5402	46.32	53.68
235-5	1.1493	0.5410	46.40	53.60
		average	**46.80**	**53.20**
		confidence limit	**0.65**	**0.65**
		SD	**0.52**	**0.52**
		RSD %	**1.11**	**0.98**

JRC code	sample mass g	residue mass g	PAC %	PA6 %
236-1	1.1836	0.5394	44.89	55.11
236-2	1.1168	0.5362	47.35	52.65
236-3	1.1556	0.5563	47.47	52.53
236-4	1.1327	0.5633	49.08	50.92
236-5	1.0520	0.4985	46.71	53.29
		average	**47.10**	**52.90**
		confidence limit	**1.88**	**1.88**
		SD	**1.51**	**1.51**
		RSD %	**3.21**	**2.86**

JRC code	sample mass	residue mass	PAC	PA6
	g	g	%	%
237-1	1.1437	0.5458	47.05	52.95
237-2	1.1307	0.5455	47.58	52.42
237-3	1.1425	0.5479	47.29	52.71
237-4	1.1279	0.5437	47.54	52.46
		average	**47.37**	**52.63**
		confidence limit	**0.39**	**0.39**
		SD	**0.24**	**0.24**
		RSD %	**0.52**	**0.46**

JRC code	sample mass	residue mass	PAC	PA6
	g	g	%	%
238-1	1.0066	0.4838	47.40	52.60
238-2	1.0014	0.4830	47.57	52.43
238-3	0.9955	0.4664	46.18	53.82
238-4	0.9944	0.4681	46.40	53.60
238-5	1.0007	0.4659	45.88	54.12
		average	**46.68**	**53.32**
		confidence limit	**0.94**	**0.94**
		SD	**0.75**	**0.75**
		RSD %	**1.62**	**1.41**

JRC code	sample mass	residue mass	PAC	PA6
	g	g	%	%
239-1	1.1212	0.5388	47.39	52.61
239-2	1.1194	0.5243	46.16	53.84
239-3	1.1184	0.5341	47.09	52.91
239-4	1.1201	0.5305	46.69	53.31
239-5	1.0964	0.5174	46.52	53.48
		average	**46.77**	**53.23**
		confidence limit	**0.60**	**0.60**
		SD	**0.48**	**0.48**
		RSD %	**1.03**	**0.90**

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Binary mixtures PP/PAC (samples 207 – 213)

JRC code	sample mass g	residue mass g	insoluble %	soluble %
207-1	1.0226	0.9799	95.70	4.30
207-2	1.0476	1.0032	95.63	4.37
207-3	1.0616	1.0155	95.53	4.47
207-4	1.0345	0.9861	95.18	4.82
207-5	1.0275	0.9814	95.38	4.62
207-6	1.0488	1.0049	95.69	4.31
207-7	1.0378	0.9883	95.09	4.91
207-8	1.0582	1.0124	95.54	4.46
207-9	1.0349	0.9872	95.25	4.75
		average	**95.44**	**4.56**
		confidence limit	**0.17**	**0.17**
		SD	**0.23**	**0.23**
		RSD %	**0.24**	**4.99**

JRC code	sample mass g	residue mass g	insoluble %	soluble %
209-1	1.0748	0.9750	90.45	9.55
209-2	1.0479	0.9517	90.56	9.44
209-3	1.0590	0.9580	90.19	9.81
209-4	1.0455	0.9489	90.50	9.50
209-5	1.1326	1.0291	90.60	9.40
209-6	1.0156	0.9207	90.39	9.61
209-7	1.0727	0.9746	90.59	9.41
209-8	1.0629	0.9650	90.53	9.47
209-9	1.0699	0.9701	90.41	9.59
209-10	1.0338	0.9398	90.65	9.35
		average	**90.49**	**9.51**
		confidence limit	**0.10**	**0.10**
		SD	**0.13**	**0.13**
		RSD %	**0.15**	**1.41**

JRC code	sample mass g	residue mass g	insoluble %	soluble %
210-1	1.2170	1.1062	90.64	9.36
210-2	1.0864	0.9868	90.57	9.43
210-3	1.0984	0.9951	90.33	9.67
210-4	1.0345	0.9399	90.59	9.41
210-5	1.1826	1.0752	90.66	9.34
210-6	1.1581	1.0471	90.14	9.86
210-7	1.2215	1.1084	90.48	9.52
210-8	1.1806	1.0745	90.76	9.24
210-9	1.1190	1.0190	90.81	9.19
210-10	1.1692	1.0624	90.60	9.40
		average	**90.56**	**9.44**
		confidence limit	**0.14**	**0.14**
		SD	**0.20**	**0.20**
		RSD %	**0.22**	**2.10**

JRC code	sample mass g	residue mass g	insoluble %	soluble %
211-1	1.0533	0.9094	85.97	14.03
211-2	1.0485	0.9040	85.85	14.15
211-3	1.0402	0.8989	86.05	13.95
211-4	1.0520	0.9081	85.95	14.05
211-5	1.0741	0.9272	85.95	14.05
211-6	1.0428	0.9007	86.00	14.00
211-7	1.0388	0.8976	86.04	13.96
211-8	1.0107	0.8724	85.95	14.05
211-9	1.0335	0.8923	85.97	14.03
		average	**85.97**	**14.03**
		confidence limit	**0.05**	**0.05**
		SD	**0.06**	**0.06**
		RSD %	**0.07**	**0.43**

JRC code	sample mass g	residue mass g	insoluble %	soluble %
212-1	1.0267	0.8857	85.89	14.11
212-2	1.0421	0.8984	85.84	14.16
212-3	1.0272	0.8863	85.91	14.09
212-4	1.0449	0.9030	86.05	13.95
212-5	1.0248	0.8842	85.91	14.09
212-6	1.0372	0.8941	85.83	14.17
212-7	1.0552	0.9100	85.87	14.13
212-8	1.0391	0.8968	85.93	14.07
212-9	1.0774	0.9300	85.95	14.05
		average	**85.91**	**14.09**
		confidence limit	**0.05**	**0.05**
		SD	**0.07**	**0.07**
		RSD %	**0.08**	**0.47**

JRC code	sample mass g	residue mass g	insoluble %	soluble %
213-1	1.1067	0.9023	81.06	18.94
213-2	1.0285	0.8505	82.24	17.76
213-3	1.0740	0.8834	81.80	18.20
213-4	1.0938	0.8925	81.13	18.87
213-5	1.1229	0.9246	81.88	18.12
213-6	1.1317	0.9341	82.09	17.91
213-7	1.0636	0.8820	82.48	17.52
213-8	1.0942	0.9025	82.03	17.97
213-9	1.0766	0.8854	81.78	18.22
213-10	0.9977	0.8225	81.99	18.01
		average	**81.85**	**18.15**
		confidence limit	**0.32**	**0.32**
		SD	**0.45**	**0.45**
		RSD %	**0.55**	**2.48**

Carpet samples PP/PAC (samples 246 – 257)

JRC code	sample mass g	residue mass g	insoluble %	soluble %
246-1	0.9785	0.8245	83.85	16.15
246-2	0.9507	0.8029	84.04	15.96
246-3	0.9607	0.8102	83.92	16.08
246-4	0.9766	0.8249	84.05	15.95
246-5	0.9673	0.8145	83.79	16.21
		average	**83.93**	**16.07**
		confidence limit	**0.15**	**0.15**
		SD	**0.12**	**0.12**
		RSD %	**0.14**	**0.74**

JRC code	sample mass	residue mass	insoluble	soluble
	g	g	%	%
246*-1	1.0650	0.7757	72.22	27.78
246*-2	1.0301	0.7518	72.37	27.63
246*-3	1.0206	0.7427	72.15	27.85
246*-4	1.0465	0.7617	72.17	27.83
246*-5	1.0521	0.7658	72.17	27.83
		average	**72.21**	**27.79**
		confidence limit	**0.11**	**0.11**
		SD	**0.09**	**0.09**
		RSD %	**0.12**	**0.32**

* PAC separated from carpet sample 246

JRC code	sample mass	residue mass	insoluble	soluble
	g	g	%	%
247-1	0.9414	0.8419	89.13	10.87
247-2	0.9649	0.8620	89.04	10.96
247-3	0.9503	0.8493	89.07	10.93
247-4	0.9657	0.8622	88.98	11.02
247-5	0.9830	0.8787	89.09	10.91
		average	**89.06**	**10.94**
		confidence limit	**0.07**	**0.07**
		SD	**0.06**	**0.06**
		RSD %	**0.06**	**0.53**

JRC code	sample mass	residue mass	insoluble	soluble
	g	g	%	%
247*-1	0.9894	0.8061	81.00	19.00
247*-2	1.1308	0.9236	81.21	18.79
247*-3	0.9993	0.8156	81.15	18.85
247*-4	0.9609	0.7847	81.19	18.81
247*-5	1.0522	0.8575	81.02	18.98
		average	**81.11**	**18.89**
		confidence limit	**0.12**	**0.12**
		SD	**0.10**	**0.10**
		RSD %	**0.12**	**0.51**

* PAC separated from carpet sample 247

JRC code	sample mass	residue mass	insoluble	soluble
	g	g	%	%
248-1	0.9386	0.8930	95.00	5.00
248-2	0.8983	0.8545	94.98	5.02
248-3	0.9019	0.8580	94.99	5.01
248-4	0.9423	0.8958	94.92	5.08
248-5	0.9246	0.8775	94.75	5.25
		average	**94.93**	**5.07**
		confidence limit	**0.13**	**0.13**
		SD	**0.10**	**0.10**
		RSD %	**0.11**	**2.00**

JRC code	sample mass	residue mass	insoluble	soluble
	g	g	%	%
248*-1	1.0771	0.9845	91.16	8.84
248*-2	1.0323	0.9442	91.22	8.78
248*-3	1.0878	0.9936	91.09	8.91
248*-4	1.0938	1.0004	91.22	8.78
248*-5	1.0872	0.9935	91.13	8.87
		average	**91.16**	**8.84**
		confidence limit	**0.07**	**0.07**
		SD	**0.05**	**0.05**
		RSD %	**0.06**	**0.62**

* PAC separated from carpet sample 248

JRC code	sample mass	residue mass	insoluble	soluble
	g	g	%	%
249-1	0.9397	0.7935	84.03	15.97
249-2	0.9231	0.7823	84.34	15.66
249-3	0.9298	0.7863	84.16	15.84
249-4	0.9590	0.8075	83.78	16.22
249-5	0.9377	0.7900	83.83	16.17
		average	**84.03**	**15.97**
		confidence limit	**0.29**	**0.29**
		SD	**0.23**	**0.23**
		RSD %	**0.27**	**1.44**

JRC code	sample mass	residue mass	insoluble	soluble
	g	g	%	%
249*-1	1.0585	0.7725	72.36	27.64
249*-2	1.0487	0.7659	72.42	27.58
249*-3	1.0482	0.7657	72.43	27.57
249*-4	1.0583	0.7730	72.43	27.57
249*-5	1.0601	0.7749	72.48	27.52
		average	**72.42**	**27.58**
		confidence limit	**0.05**	**0.05**
		SD	**0.04**	**0.04**
		RSD %	**0.06**	**0.15**

* PAC separated from carpet sample 249

JRC code	sample mass	residue mass	insoluble	soluble
	g	g	%	%
250-1	1.0510	0.9461	89.74	10.26
250-2	1.1446	1.0253	89.28	10.72
250-3	1.1050	0.9927	89.55	10.45
250-4	1.0802	0.9692	89.43	10.57
250-5	1.1322	1.0143	89.29	10.71
		average	**89.46**	**10.54**
		confidence limit	**0.24**	**0.24**
		SD	**0.19**	**0.19**
		RSD %	**0.21**	**1.80**

JRC code	sample mass	residue mass	insoluble	soluble
	g	g	%	%
250*-1	1.0339	0.8466	81.42	18.58
250*-2	1.0435	0.8546	81.43	18.57
250*-3	1.0364	0.8502	81.57	18.43
250*-4	1.0463	0.8569	81.43	18.57
250*-5	1.0471	0.8586	81.53	18.47
		average	**81.48**	**18.52**
		confidence limit	**0.09**	**0.09**
		SD	**0.07**	**0.07**
		RSD %	**0.09**	**0.38**

* PAC separated from carpet sample 250

JRC code	sample mass	residue mass	insoluble	soluble
	g	g	%	%
251-1	1.1459	1.0899	94.97	5.03
251-2	1.1015	1.0479	94.99	5.01
251-3	1.0929	1.0380	94.83	5.17
251-4	1.1059	1.0520	94.98	5.02
251-5	1.1068	1.0558	95.25	4.75
		average	**95.00**	**5.00**
		confidence limit	**0.19**	**0.19**
		SD	**0.15**	**0.15**
		RSD %	**0.16**	**3.10**

JRC code	sample mass g	residue mass g	insoluble %	soluble %
251*-1	1.0021	0.9161	91.17	8.83
251*-2	1.0067	0.9206	91.20	8.80
251*-3	1.0064	0.9189	91.06	8.94
251*-4	1.0199	0.9321	91.14	8.86
251*-5	1.0494	0.9591	91.15	8.85
		average	**91.14**	**8.86**
		confidence limit	**0.07**	**0.07**
		SD	**0.05**	**0.05**
		RSD %	**0.06**	**0.61**

* PAC separated from carpet sample 251

JRC code	sample mass g	residue mass g	insoluble %	soluble %
252-1	1.0652	0.8978	83.87	16.13
252-2	1.1356	0.9581	83.96	16.04
		average	**83.91**	**16.09**
		confidence limit	**0.55**	**0.55**
		SD	**0.06**	**0.06**
		RSD %	**0.07**	**0.38**

JRC code	sample mass g	residue mass g	insoluble %	soluble %
252*-1	1.3084	0.9531	72.23	27.77
252*-2	1.3105	0.9551	72.26	27.74
252*-3	1.2925	0.9415	72.22	27.78
		average	**72.24**	**27.76**
		confidence limit	**0.05**	**0.05**
		SD	**0.02**	**0.02**
		RSD %	**0.03**	**0.08**

* PAC separated from carpet sample 252

JRC code	sample mass g	residue mass g	insoluble %	soluble %
253-1	1.0612	0.9500	89.23	10.77
253-2	1.0658	0.9538	89.20	10.80
		average	**89.21**	**10.79**
		confidence limit	**0.19**	**0.19**
		SD	**0.02**	**0.02**
		RSD %	**0.02**	**0.20**

JRC code	sample mass g	residue mass g	insoluble %	soluble %
253*-1	1.3063	1.0684	81.32	18.68
253*-2	1.2984	1.0620	81.33	18.67
253*-3	1.2969	1.0605	81.30	18.70
		average	**81.32**	**18.68**
		confidence limit	**0.03**	**0.03**
		SD	**0.01**	**0.01**
		RSD %	**0.01**	**0.06**

* PAC separated from carpet sample 253

JRC code	sample mass g	residue mass g	insoluble %	soluble %
254-1	1.0655	1.0128	94.91	5.09
254-2	0.9837	0.9371	95.12	4.88
		average	**95.01**	**4.99**
		confidence limit	**1.36**	**1.36**
		SD	**0.15**	**0.15**
		RSD %	**0.16**	**3.05**

JRC code	sample mass g	residue mass g	insoluble %	soluble %
254*-1	1.2447	1.1401	91.35	8.65
254*-2	1.3006	1.1924	91.44	8.56
254*-3	1.2007	1.0915	90.65	9.35
		average	**91.15**	**8.85**
		confidence limit	**1.08**	**1.08**
		SD	**0.44**	**0.44**
		RSD %	**0.48**	**4.93**

* PAC separated from carpet sample 254

JRC code	sample mass g	residue mass g	insoluble %	soluble %
255-1	1.1146	0.9426	84.16	15.84
255-2	1.1133	0.9422	84.22	15.78
255-3	1.1551	0.9778	84.24	15.76
255-4	1.1532	0.9767	84.29	15.71
255-5	1.1090	0.9384	84.21	15.79
255-6	1.1176	0.9462	84.26	15.74
		average	**84.23**	**15.77**
		confidence limit	**0.05**	**0.05**
		SD	**0.04**	**0.04**
		RSD %	**0.05**	**0.28**

JRC code	sample mass g	residue mass g	insoluble %	soluble %
256-1	1.1349	1.0161	89.24	10.76
256-2	1.1084	0.9931	89.30	10.70
256-3	1.1065	0.9918	89.34	10.66
256-4	1.1466	1.0281	89.37	10.63
256-5	1.0987	0.9856	89.42	10.58
		average	**89.33**	**10.67**
		confidence limit	**0.08**	**0.08**
		SD	**0.07**	**0.07**
		RSD %	**0.08**	**0.64**

JRC code	sample mass g	residue mass g	insoluble %	soluble %
257-1	1.0111	0.9609	94.89	5.11
257-2	1.0957	1.0412	94.88	5.12
257-3	1.0246	0.9729	94.80	5.20
257-4	1.0881	1.0340	94.88	5.12
257-5	1.1376	1.0809	94.87	5.13
257-6	1.0391	0.9865	94.79	5.21
		average	**94.85**	**5.15**
		confidence limit	**0.05**	**0.05**
		SD	**0.04**	**0.04**
		RSD %	**0.05**	**0.84**

European Commission

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Abstract
In August 2007, the European Commission's Joint Research Centre (JRC) was entrusted by DG Enterprise to verify the validity and applicability of the testing methods, proposed by Aquafil S.p.A., for the identification and quantification of their new fibre (PAC). Developed for carpet applications, the fibre contains polyamide fibrils in polypropylene matrix (islands-in-the-sea).
Experimental results confirmed that identification of PAC can be achieved using Scanning Electronic Microscope (SEM) analysis, after dissolving the polyamide fibrils with formic acid. Additionally, Fourier Transform Infrared Spectroscopy (FT-IR) and Differential Scanning Calorimetry (DSC) can be used as techniques to differentiate PAC from binary mixtures made of polypropylene (PP) and polyamide (PA) fibres.
For quantification purposes, experiments showed that ventilated oven can be used, instead of the vacuum one proposed by the applicant, without damaging the fibre. The normal pre-treatment described in Directive 96/73/EC, was proved to be applicable to PAC and its correction factor *b* for mass loss during pre-treatment was established (0 %). The *agreed allowance* of the new fibre was measured (0.40 %) and the established value, adopted by the European network of national experts on Textile Labelling (ENNETL), was 1.00 %. The solubility properties of PAC were evaluated with all methods described in Directive 96/73/EC. The solubility behaviour of PA6 and PP was studied as well, in case the information is not included in the same Directive. The new fibre was insoluble in methods 1, 2, 5-11 and 14. The *d* correction factors were established on the basis of the experimental work carried out by the JRC and, in the case of methods 2, 8 and 11, confirmed through a collaborative trial at European level. The resulting values were: 1.00 for methods 1, 2, 5, 6, 8-10, 1.005 for method 11 and 1.01 for methods 7 and 14. PP was insoluble in methods 1, 3, 5-11, 14 and 16; the average *d* factor values were 1.00 in all cases. PA6 was insoluble in methods 5 and 10 and the average *d* factor values were 1.00 and 1.01, respectively. Experts agreed that only the correction factors *d* for PAC and PP shall be inserted in Directive 96/73/EC, as the ones for PA were measured only on PA6.
For the quantification of PA in PAC, the three methods proposed by the applicant (hydrolysis, DSC and FTIR) were examined by the JRC. Additionally, a series of chemical dissolution methods were investigated in order to find accurate and less time-consuming alternative methods for this quantification. PA in PAC was quantified *via* elemental analysis, on the basis of the nitrogen content of PAC samples, to obtain results that could be considered as reference values. Among the tested methods, method 16 of Directive 96/73/EC was proved to be the most accurate and non time-consuming. It was, therefore, proposed by the JRC and agreed by experts as the suitable method to quantify PA in PAC.
For the quantification of PAC in binary mixtures, manual separation is an adequate technique, whenever applicable. Several alternative methods were studied for mixtures with PP or PA and their accuracy evaluated by comparison of quantitative results to the reference values obtained *via* manual separation. Method 16 of Directive 96/73/EC was proved to be accurate for the quantification of binary mixtures PP/PAC; however, this quantification can only be achieved if the PA content of PAC is known or a quantity of PAC can be separated and analysed. Method 11 of Directive 96/73/EC was considered very accurate for the quantification of binary mixtures PA/PAC and was proposed by the JRC. As agreed during the 10th ENNETL meeting, a collaborative trial was organised by the JRC to validate method 11, in accordance with the rules laid down in ISO 5725 (1994). On the basis of successful results, experts agreed that the field of application of method 11 in Directive 96/73/EC shall be extended to the quantification of binary mixtures PA/PAC. Moreover, the modified washing procedure, needed to achieve a correct quantification of binary mixtures with high percentages of PA fibres, shall be added in the method's description together with the established precision of the analytical method, expressed as reproducibility limit (2 %).
Based on experimental results, discussions during the 9th, 10th and 11th ENNETL meetings and written consultation with national experts, the name and definition agreed and proposed for the new fibre were "polypropylene/polyamide bicomponent: a bicomponent fibre composed of between 10 % and 25 % by mass of polyamide fibrils embedded in polypropylene matrix".

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